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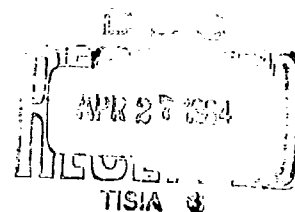
## INVESTIGATION OF THE FLASHING OF AEROSOLS

### FINAL REPORT

18 March 1963 - 17 April 1964

Contract No. DA 18-108-AMC-118(A)

M.R.I. Project No. 2685-C



For

U. S. Army Chemical Research and  
Development Laboratories  
Edgewood Arsenal, Maryland

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Covering the Period

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Prepared by

Alan R. Pittaway

20 April 1964

## PREFACE

This is the Final Report on Contract No. DA 18-108-AMC-118(A), M.R.I. Project 2685-C, titled "Investigation of the Flashing of Aerosols." It covers the period 18 March 1963 through 17 April 1964. All information presented in the monthly letter reports and the project quarterly reports is contained in this report.

The purpose of this project was to obtain information on aerosol flammability as a function of (a) fuel concentration, vapor pressure and particle size, (b) source of ignition, and (c) composition of the environmental gas. Additives which will tend to suppress either the ignition or the combustion of the aerosol were evaluated.

This one-year project was sponsored by the U. S. Army Chemical Research and Development Laboratories, Director of Weapons Systems, Physico-chemical Research Division, Colloid Branch. Mr. Joseph Pistrutto was the Project Officer and Mr. Jerome Goldenson, Deputy Project Officer. Work on this program was accomplished by Mr. Alan R. Pittaway, the principal investigator, Mr. Harry Pollock, Mr. Frank Brink, Mr. Fred Bergman, Mr. Roger Schroeder, Mr. Richard Fetter, and Mr. Kenneth Doll under the supervision of Dr. John W. Barger, Assistant Director, Chemistry Division.

Approved for:

MIDWEST RESEARCH INSTITUTE



F. V. Morris, Director  
Chemistry Division

20 April 1964

# TABLE OF CONTENTS

	<u>Page No.</u>
Summary . . . . .	1
I. Introduction . . . . .	2
II. Analysis of the Problem . . . . .	2
A. Potential Aerosol Ignition Sources . . . . .	2
B. Aerosol Combustion Phenomena . . . . .	12
C. Summary . . . . .	12
III. Method of Approach . . . . .	13
A. Influence of Detonation Product Combustion . . . . .	14
B. Shock Wave Ignition . . . . .	15
C. Miscellaneous Ignition Sources . . . . .	16
D. Use of Agent Combustion Inhibitors . . . . .	17
E. Summary of Research Program . . . . .	18
IV. Materials and Equipment . . . . .	20
A. Establishment of the Detonation Product Gas Mixture . . . . .	20
B. Candidate Aerosol Materials . . . . .	21
C. Combustion Chamber Design and Fabrication . . . . .	28
D. Shock Tube Design and Fabrication . . . . .	38
V. Experimental Data . . . . .	49
A. Particle Size Determination . . . . .	49
B. Combustion Chamber Studies . . . . .	52
C. Shock Tube Studies . . . . .	58
D. Hot Particle Ignition . . . . .	58
E. Combustion Inhibition Studies . . . . .	62
VI. Discussion and Conclusions . . . . .	62
A. Experimental Results . . . . .	62
B. Use of QL . . . . .	63
C. Aerosol Generation . . . . .	63
VII. Recommendations . . . . .	64
Bibliography . . . . .	65
Symbol List . . . . .	66

TABLE OF CONTENTS (Continued)

List of Tables

<u>Table</u>	<u>Title</u>	<u>Page No.</u>
I	Composition of Explosives in Mole Per Cent . . . . .	3
II	Variation in Detonation Products of TNT at Three Loading Densities . . . . .	4
III	Detonation Products of Explosives at a Loading Density of 1.6 G/CC . . . . .	5
IV	Particle Sizes as a Function of Pump Pressure . . . . .	51
V	Hot Particle Ignition . . . . .	61

List of Figures

<u>Figure</u>	<u>Title</u>	<u>Page No.</u>
1	Variation of Flash Point with Boiling Point of Aliphatic Hydrocarbons . . . . .	23
2	Variation of Flash Point with Boiling Point of Aliphatic and Alkanol Amines . . . . .	24
3	Over-All View of Combustion Chamber Showing All Accessory Equipment and Facilities . . . . .	30
4	Over-All View of Combustion Chamber Showing All Accessory Equipment and Facilities . . . . .	31
5	Aerosol Injection System Showing Method of Isolating QL from Atmosphere . . . . .	33
6	Schematic of Combustion Chamber System Showing Gas Lines . . .	35
7	Circuit Diagram of Spark Igniter . . . . .	36
8	A Shock Wave Time-Travel Diagram . . . . .	39

TABLE OF CONTENTS (Concluded)

List of Figures (Concluded)

<u>Figure</u>	<u>Title</u>	<u>Page No.</u>
9	Shock Tube Pressure and Temperature Ratios vs. Incident Shock Wave Mach Number . . . . .	43
10	Constants for Evaluation of "Pulse" Times for Helium Driver Gas . . . . .	43
11	Constants for Evaluation of "Pulse" Times for Nitrogen Driver Gas . . . . .	44
12	Minimum Receiver Lengths to Avoid Reflected Shock Waves from Contact Surface . . . . .	44
13	Over-All View of 4-in. I.D. Shock Tube . . . . .	46
14	Instrumentation for 4-in. I.D. Shock Tube . . . . .	47
15	Driver Section, 4-in. I.D. Shock Tube, Showing Device for Breaking Diaphragms . . . . .	48
16	Flammability Envelope of Three Component Systems . . . . .	57

### SUMMARY

This program is concerned with determining flammability of aerosol systems. A complete review of the agent flashing problem is presented together with an analysis of the problem as a whole. A constant pressure combustion chamber and a shock tube were constructed to study aerosol flammability. Studies were conducted with QL-air aerosols, detonation product gas-air mixtures, and the three component detonation product gas-QL-air system. The data show that the system flammability is dictated by the detonation product gas-air flammability and is not significantly affected by the aerosol phase.

Moderate strength shock waves will ignite the system but hot metal and glowing carbon particles will not, under the conditions tested. The QL aerosol-air mixture is easily ignited by flame but not by spark. QL aerosol-air mixtures burn with difficulty due to inhibition of the combustion by the products of combustion.

The data support the hypothesis that the combustion of the detonation product gas is the primary aerosol flashing ignition source. It also supports the contention that the aerosol burns (in the general case) only in the presence of the combusting product gas mixture.

Recommendations are made to continue the study using other aerosol materials and to investigate direct aerosol combustion and ignition inhibition.

This report is complete in itself and encompasses all information included in any prior letter or quarterly report.

## I. INTRODUCTION

This program is related to the phenomenon known as "flashing" which occurs during the explosive dissemination of combustible liquids. An analysis of the flashing phenomenon is given below. The purpose of this project is to provide additional fundamental information on aerosol combustion. The information can then be applied to specific flashing problems.

A large, electrically ignited, "combustion chamber" was used to determine the interrelationships between aerosol-fuel-particle size, concentration, vapor pressure, and environmental gas composition on aerosol flammability. A shock tube was used to evaluate the shock strength required to ignite mixtures found to be flammable in the combustion chamber.

This report reviews the current status of the project and covers its development since the start of the program.

## II. ANALYSIS OF THE PROBLEM

An analysis of aerosol flashing inhibition during explosive dissemination must be divided into two parts: (a) the ignition-source parameters, and (b) the suppression of aerosol combustion. These factors are interrelated, since the characteristics of the ignition may dictate the most favorable method for inhibition of the aerosol.

### A. Potential Aerosol Ignition Sources

In the explosive dissemination of agents there are a number of possible ignition sources. All but one are related either to the explosive used or to the ammunition shell casing. These are in probable order of decreasing importance:

1. Ignition by combustion of the detonation products,
2. Ignition by contact with the hot detonation products,
3. Ignition by shock waves generated by:
  - a. The burster charge,
  - b. The explosion of an adjacent shell, or
  - c. Shell fragments.



4. Ignition by electrical static discharge to relieve static potential developed when droplets move through the atmosphere, and

5. Ignition from hot shell fragments.

These are discussed below, at greater length, and in the same order.

1. Ignition by detonation product combustion: The burster charges used in chemical shell ammunition are usually Tetryol or Composition B. Tetryol is composed of 35 per cent TNT and 65 per cent tetryl; Composition B of 55 per cent RDX, 40 per cent TNT, and wax.

a. Detonation products of explosives: Explosives can be classified in terms of their oxygen balance, i.e., the degree to which the detonation products are completely oxidized at the completion of the detonation process. TNT has a high negative oxygen balance. Under favorable conditions for a secondary explosion of the products of detonation of TNT with air, an explosion producing a heat of explosion of 2,500 kcal per gram of the original TNT might result. Hence, this secondary explosion could release nearly three times as much energy as the original primary explosion.<sup>1/</sup> Secondary explosions of this type are well known. Tetryl also has a negative oxygen balance while that of RDX is slightly positive. The compositions of these three primary explosives, together with Tetryol and Composition B, are given in Table I in mole per cent.

TABLE I

COMPOSITION OF EXPLOSIVES IN MOLE PER CENT

<u>Explosive</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>	<u>Oxygen</u>
RDX	16.20	2.70	37.80	43.20
Tetryl	29.28	1.74	24.36	44.64
TNT	36.96	2.20	18.48	42.24
Tetryol	31.97	1.90	22.30	43.80
Composition B	23.70	2.38	28.20	40.70

Tetryol and Composition B also have a negative oxygen balance, and Tetryol is more negative than Composition B.

The density to which an explosive containing TNT is compressed has a profound influence on the detonation products. This factor can be even more important than the oxygen balance in determining the combustibility of the products. Table II shows the wide variation obtainable.

TABLE II

VARIATION IN DETONATION PRODUCTS OF TNT  
AT THREE LOADING DENSITIES

<u>Moles/kg</u>	<u>Loading Density, g/cc</u>		
	<u>0.6</u>	<u>1.0</u>	<u>1.6</u>
CO	22.0	16.8	9.4
CO <sub>2</sub>	1.5	3.5	6.8
H <sub>2</sub>	5.1	2.5	0.6
H <sub>2</sub> O	1.5	2.6	3.4
N <sub>2</sub>	5.7	5.5	5.0
CH <sub>4</sub>	1.3	1.9	2.2
NH <sub>3</sub>	0.2	0.8	1.1
HCN	3.0	1.4	2.0
C	3.0	7.1	10.4

Table II indicates that, as the loading density increases, the CO<sub>2</sub> and C concentrations increase while the CO concentration decreases. Other factors being equal, increasing the loading density should reduce the ignitibility of the decomposition products and thus reduce secondary burning.

Tetryl and RDX exhibit similar changes in detonation products as a function of loading density.

In summary, all explosives with a negative oxygen balance produce very combustible detonation products. The combustibility, ignitibility, and composition of these products are strongly dependent on the loading density of the explosive charge. Table III illustrates further the magnitude of these phenomena by comparing TNT, tetryl, and RDX at a single loading density. Even though these materials differ significantly in oxygen balance, each produces large quantities of combustibles.

TABLE III

DETONATION PRODUCTS OF EXPLOSIVES AT A  
LOADING DENSITY OF 1.6 G/CC

<u>Moles/kg</u>	<u>TNT</u>	<u>Tetryl</u>	<u>RDX</u>
CO	9.4	10.6	8.0
CO <sub>2</sub>	6.8	6.6	5.5
H <sub>2</sub>	0.6	0.5	1.3
H <sub>2</sub> O	3.4	2.2	8.0
N <sub>2</sub>	5.0	7.0	12.1
NH <sub>3</sub>	1.1	0.9	2.8
HCN	2.0	2.9	-
CH <sub>4</sub>	2.2	1.6	-
C	10.4	2.7	-

The empirical assumption that improving the oxygen balance should reduce detonation product combustibility is only partly true. The loading density will determine the oxygen equilibrium between CO and CO<sub>2</sub> and will control the quantity of free carbon formed. Thus an oxygen-rich explosive at low loading density could produce as much combustible CO as an oxygen-poor explosive at a high loading density. On this basis, the tendency for secondary combustion of the detonation products would be the same.

There are two additional factors which influence the tendency for the detonation products to burn in a given system: the detonation temperatures produced and the brisance of the explosive. An increase in either increases the potential for ignition. Therefore, while it may be possible to lower the quantity of combustible products by changing the explosive oxygen balance, this may not eliminate the tendency of the products to burn if the detonation temperature or brisance are simultaneously increased.

In summary, the kind of explosive and the conditions under which it is detonated determine the tendency for the detonation products to burn with air after the explosion.

b. Summary of significant experimental data: In a recent series of firings at Dugway Proving Ground during 1951 - 1961, attempts were made to correlate aerosol flashing to the time duration of the flash (as measured by IR sensors and photographically), the burster-to-agent weight ratio, and type of burster charge. Standardized bursters were apparently used in most instances.

In the majority of instances, when Tetryol bursters were used, the flash time varied from 0.002 to 0.007 sec. A second grouping of flash times occurred in the interval of 0.02 to 0.04 sec. The percentage of agent recovered did not correlate with the flash times in any manner, i.e., large recoveries were observed at flash times of 0.35 sec. and small recoveries at flash times of 0.002 sec. and vice versa. In a comparison test of Composition B and Tetryol, the flash times for Composition B varied from 0.6 to 0.06 sec. Compared to the Tetryol burster, the longer flash times did correlate with lower agent recovery, i.e., approximately 60 per cent for Tetryol and 10 per cent for Composition B.

In another series of tests, using a water-filled 115-mm. rocket with a Tetryol burster, the flash duration was 0.002 to 0.005 sec., indicating that the flash observed in the majority of instances with a Tetryol burster was primarily due to the burster alone.

A further observation on the results of the tests is that increasing the agent-to-burster weight ratio decreased the amount of agent lost.

Before a discussion of the above data in relation to the burster as the primary ignition source for aerosol flashing can be undertaken, several other bits of information are needed. First, there is a relationship between agent loss and case strength. These data have appeared in a number of Army Chemical Center, Stanford, and Aerojet General reports. Second, agent loss can be minimized if the burster is surrounded by agent or if oxygen is excluded from the shell. These data appear both in Aerojet and Stanford reports. Third, high humidity inhibits combustion of the aerosol. Fourth, carbon tetrachloride around the burster tends to prevent flashing whereas brominated compounds are not as effective. This datum is from Aerojet General reports.

c. New interpretation and correlation of data: The explosion of burster charge explosives produces large quantities of combustible gases. The component of these gases, present in largest amount, is CO. When mixed with atmospheric oxygen, these gases form a highly combustible mixture which can be ignited with almost no added energy for activation. During the initial expansion of these gases and their mixture with air, they progress through a fuel/oxidant range from rich to lean. Unfortunately, CO is capable of forming explosive mixtures with air almost up to 100 per cent CO concentration,<sup>2/</sup> so that this gas is capable of combustion with air throughout the expansion of the detonation products until the CO concentration is less than about 12 per cent.

If it is assumed, for the sake of argument, that aerosol flashing is caused by the secondary burning of the burster explosive detonation products with air, then all of the above data fall neatly into place.

The flash duration observed when water was used as a filler is approximately the same as that observed when using an agent (both tests used a Tetryol burster). This fact indicates that the combustion of the agent occurs during the combustion of the detonation products, and that the aerosol cloud does not burn except when surrounded by the detonation product flame gases. Undoubtedly there are exceptions to this, but the normal loss of agent when Tetryol bursters are used occurs from this source. The Tetryol burster secondary combustion may produce aerosol combustion which is just below the critical value for ignition of total combustion of the aerosol-air cloud. This would tend to explain the wide variation in results experienced with Tetryol bursters.

The phenomenon observed when Composition B bursters are used presents a paradox. Composition B has a significantly lower negative oxygen balance than Tetryol. This should produce a smaller quantity of combustible detonation products and decrease agent loss. Since agent loss was increased with Composition B bursters, this suggests that one of two other phenomena may have been involved. The Composition B burster may have had a materially different loading density, thus changing the carbon monoxide to solid carbon ratio in favor of creating a more combustible mixture. On the other hand, this unusual behavior may signify that the chemical agent reacts with the oxygen in the detonation products and that agent destruction would be reduced by lowering the quantity of oxygen in the explosive.

The increased agent lost when the case strength (thickness) is increased is caused by the slightly longer time given to the detonation products before adiabatic expansion into the atmosphere. This slight delay allows the gases to come to better chemical equilibrium with the resultant production of additional CO. The greater CO concentration tends to produce a more severe secondary combustion with greater loss of agent.

If the burster is surrounded by agent, and/or oxygen is excluded from the shell, the expanding cloud of detonation products is prevented from mixing with oxygen until such time that the cloud expands to below either its self-ignition temperature or beyond its flammability limit. This physical configuration could also produce the phenomenon of direct inhibition of the CO-air flame by hydrocarbons of the CW agent system. This inhibition can be either chemical or physical since both forms are known. The increased

loss of agent noted when the shell end closures are weaker than the shell casing is a related phenomenon. A weak end closure tends to cause separation of a portion of the detonation gases from the agent, allowing the gases to jet into the atmosphere from the case end in a manner most favorable for ignition of the gas-air cloud. Increasing the agent-to-burster weight ratio accomplishes the same thing as insuring that the agent surrounds the burster charge, i.e., it makes it easier to insure that combustion of the detonation gases is prevented.

As has been noted in the Aerojet reports, high atmospheric humidity tends to prevent aerosol flashing. Water vapor causes a rapid reduction in the upper flammability limit of CO with air,<sup>3/</sup> thus tending to prevent secondary combustion of the detonation products. These same reports noted that CCl<sub>4</sub> was a better suppressing agent than bromine compounds. This conclusion is surprising since hydrocarbon combustion usually is inhibited much more by bromine than by chlorine. However, carbon monoxide-air combustion, as we have been discussing here, is inhibited more by chlorine than by bromine compounds, and CO is almost unique in this respect. For example, 1.16 per cent of CCl<sub>4</sub> will render CO nonflammable in air<sup>4/</sup> but it requires 6.2 per cent methyl bromide<sup>5/</sup> to accomplish the same task. Compare these data to that of a methane-air system; in this case it requires 13 per cent CCl<sub>4</sub> but only 4.7 per cent methyl bromide to prevent combustion.<sup>5/</sup>

d. Summary: There is a large body of evidence to indicate the burning of the burster detonation products as the chief culprit in aerosol flashing. The indications are that the combustion of the detonation products of the burster charge serves either to ignite the aerosol-air cloud, or to pyrolyze the agent during the combustion of the detonation products with air. This flashing can be prevented or minimized by

- (1) Reducing the flammability of the detonation product gases,
- (2) Changing the physical configuration of the agent and burster and/or the weight ratio, and
- (3) Incorporating suitable inhibitors into the system.

This last factor is of major importance, and the reader is reminded that previous data show that the type of inhibitor used is of major importance.

2. Ignition by contact with detonation products: The ignition of high boiling-point hydrocarbon aerosols exhibits some interesting phenomena. There are a number of references to this but two bearing directly on the problem will serve to illustrate the point. Armour found that aerosols of moderately large particle sizes could not be ignited by spark energies up to

786 joules or exploding wire energies up to 468 joules. The aerosols were readily ignited by a 1-1/2 in. gas flame, a Nichrome wire shorted across 110 v., or a platinum or iron wire heated above 1016°C. Pistritto in an earlier investigation found essentially the same phenomena. The obvious trap of not allowing sufficient gap between the spark or exploding wire electrodes can be ruled out as Pistritto mentions this phenomenon in his report.

The data in the preceding paragraph imply a free radical mechanism of aerosol ignition and combustion. Pyrolysis of the simulants used, by sparks and exploding wires, did not produce sufficient quantities of molecular fragments to initiate the reaction. Flames produce the required chain carriers and initiators directly; therefore, a much lower rate of energy input, comparatively, is required for ignition. Hot wires produce pyrolysis products which can be significantly different from those of sparks and exploding wires. They can also be catalytic surfaces for reaction initiation; iron can be the equivalent of platinum in this regard.<sup>6/</sup>

Initially the explosive detonation products are rich in free radicals. There are considerable quantities of NO and OH radicals as well as H and O atoms. These are rapidly destroyed, within a few hundred microseconds of the detonation. Some of these, particularly OH, are remarkably long-lived, requiring several milliseconds for complete recombination when the concentration is large. These radicals therefore have the potential of initiating aerosol-air combustion.

A second process can also occur. The detonation product gases initially are at a temperature of 2000°C to 3000°C. As these reacting gases move out through the chemical agent, direct reaction with the agent as well as pyrolysis of the agent can occur. Gas at this temperature can also cause autoignition of air-aerosol mixtures.

3. Shock wave ignition of aerosols: Shock waves are a potent source of thermal energy. The compressive force exerted is easily capable of causing pyrolysis of fuels and generation of free radicals.

There is no doubt that shock waves have the potential of causing ignition in a combustible system, and they are the proven cause of the phenomenon known as gun flash. When the propellant gases of a small arms or artillery weapon issue into the atmosphere, a standing shock wave is set up at the muzzle. This shock wave marks the line of demarcation between subsonic and supersonic flow. The gas in passing through this shock is strongly heated and compressed as kinetic energy is converted to heat. These gases expand, cool, and form an explosive mixture with the atmosphere, which is then ignited by hot gas and/or free radicals at the shock front. When this shock wave is destroyed, either by a nozzle or a bar-type suppressor, ignition is prevented and no flash occurs.

a. Shock waves from burster explosion: The most potent shocks available as ignition sources are those produced by the burster explosion. There are two shocks formed, the detonation shock and the "pressure wave" shock. Unfortunately, there is little information available at this instant to determine the relationship between the chemical agent filler and the movement of the detonation shock wave. If the agent moves an appreciable distance riding the surface of this wave, then there may be sufficient time to form an ignitable aerosol mixture. This does not seem to be too probable. The shock wave formed by the detonation has to be the agent responsible for the shell case rupture, and this action places it ahead of the agent filling at the moment of aerosol generation.

A different sequence of action occurs with the second shock wave. The detonation product gas molecules are initially receding from each other at sonic velocity, but are traveling at supersonic velocity with respect to the surrounding atmosphere and chemical agent. As these gases expand, they will overtake the surrounding agent filler, thus causing a shock wave to penetrate through the expanding agent after some mixture with air has occurred. This shock wave then could trigger aerosol flashing. The second shock, called a pressure wave, contains more net energy than the detonation wave.

The pressure-wave shock could also be the source of secondary ignition of the detonation products with air. The initial supersonic movement of the detonation product gases with respect to air does not allow penetration of the air across the shock front. The air essentially piles up, is heated by compression, and rides the surface of the wave. At about 20 to 50 times the original explosive diameter, the pressure in the product gases falls to one atmosphere and this shock front "breaks away" through the compressed air front causing additional heating in the initial product gas-air mixture, resulting in ignition. At properly chosen camera angles, high-speed photographs of the shell burst (2 in. diameter burster) would show the expanding dark cloud (carbon particles) until its diameter was about 8 ft. At that point "break away" would occur and ignition could be observed at the air-gas interface, propagating through the remainder of the cloud.

There is a reservoir of untapped information available on the reaction of liquids under the influence of explosively generated shock waves, in the field of explosive forming of metals. An examination of these data should provide much fruitful information regarding the validity of the above hypothesis.



b. Shock wave from shell fragments: The initial burster explosion can produce shell fragments moving at velocities in excess of 2,000 ft/sec. The supersonic velocity of these missiles creates a shock wave which is equivalent to the bow wave of a small arms bullet. These shocks are energetically of low order and there are no known recorded examples of such a shock causing ignition of combustible gases, even under the most favorable circumstances. For example, a 0.30 caliber bullet fired through a balloon filled with hydrogen and oxygen will not cause ignition.

c. Shock waves from adjacent shell bursts: As noted in section (a) above, the burster charge creates a strong shock wave. If two or more charges are exploded simultaneously, as in a mine field, the shock wave created by an adjacent charge moving through the aerosol cloud could cause ignition. In addition, the line of intersection of two colliding shock waves would produce even more favorable conditions for ignition of an aerosol.

4. Ignition by static discharge: Dust and liquid droplets can acquire a high voltage charge by virtue of their movement in an air stream. Potential differences of 100,000 v. are possible. It is conceivable that a static discharge in an aerosol cloud could produce ignition. Ignition by static discharges in dust clouds is a well recognized hazard in many industries. However, it has been shown experimentally that aerosols of high-boiling liquids are difficult to ignite by spark discharges. Ignition by a static discharge is therefore considered possible but not probable.

5. Ignition by hot-shell fragments: Functioning of a chemical projectile or mine results in considerable mechanical work on the shell case. The detonation wave exerts force causing rupture and fragmentation. Much of this work then appears as heat in the shell fragments. After case rupture, these fragments are given considerable velocity and shock waves are formed as they move through the atmosphere.

It is difficult to see how these fragments could impart their latent heat to the aerosol cloud. The shock front and boundary layer tends to prevent gaseous material from reaching the surface. Some liquid and solid particles with sufficient mass might have enough inertia to penetrate the front, but these would then be trapped inside the boundary layer surrounding the fragment.

Actually, the shock wave created by the fragment velocity is probably a much more potential ignition source than the heat from the fragment itself. Temperatures in this shock front could be much higher than the fragment temperature.

## B. Aerosol Combustion Phenomena

There are two types of combustion involved in the burning of aerosols, (1) the diffusive burning of large drops, and (2) "premixed vapor" type burning of small drops.

Burgoyne and co-workers have identified the small droplet size as being below 10 microns and the large droplet size as above 40 microns, with a mixture of the two types of burning occurred for intermediate particle sizes. Work by Armour Research on higher boiling liquids than those used by Burgoyne indicated that the upper limit drop size tended to increase to between 50 and 100 microns. These data also suggest that the lower limit drop size was similarly suppressed.

The initiation of the diffusive burning of larger drops occurs in either a fuel-rich or a fuel-lean mixture. The droplet is surrounded by a vapor cloud and ignition occurs at the vapor-air mixture strength which is just able to support combustion. After ignition the subsequent combustion occurs in all mixtures within the flammability limits. For large drops, diffusion and not chemical kinetics is the rate-controlling process. Therefore, the burning of such drops produces merely a diffusion flame of vapor and air.

The burning of small drops can occur at any fuel/oxidant ratio from fuel-rich to lean since the combustion is primarily that of a premixed vapor in air. The burning rate process is controlled by chemical kinetics, and the flammability limits will be essentially the flammability limits of the pure vapor-air system.

## C. Summary

The aerosol flashing problem can be analyzed as one or more of the following combustion systems:

1. Combustion of the air-aerosol mixture but only during combustion of the detonation products with air.
2. Pyrolysis of the aerosol during combustion of the detonation products with air.
3. Combustion reaction of the aerosol with the detonation product gases.

4. Pyrolysis of the aerosol while in contact with the detonation product gases.

5. Combustion of the aerosol with air alone.

The ignition sources for these systems are shock waves, spontaneous ignition of either the detonation products or the aerosol, combustion of the detonation products, or contact with hot metal fragments. These ignition sources can be broken down as possibly acting in a sequential form rather than independently. Thus for number one above, a shock wave could ignite the detonation products which in turn ignites the aerosol, etc. The present evidence, subject to experimental verification, indicates strongly that the detonation product gases are intimately involved in the problem and that elimination of their combustion would greatly reduce or eliminate aerosol flashing.

There is no doubt that in some cases the agent aerosol does combust with air. When this occurs, the aerosol combustion can be simplified to two characteristic types, a diffusion flame with air surrounding each fuel droplet and/or a vapor phase "premixed flame" type system, both of which can vary from fuel-rich to fuel-lean.

Inhibition of combustion must take into consideration the peculiarities of the system and particularly the mode of ignition. Ideally, the inhibitor should act to suppress the ignition of the detonation products (for case 1 above), but be capable of incorporation into the chemical agent for dispersion. Suppression of detonation product ignition would also reduce the exposure of the chemical agent to thermal decomposition processes.

Selection of an inhibitor also must be based on the fact that three different combustion systems are involved, i.e., detonation products with air, an agent diffusion flame, a rich and/or lean agent premixed flame, and various mixtures of all three.

### III. METHOD OF APPROACH

Our analysis of the problem led to the establishment of an initial working concept of flashing. This concept stated that aerosol ignition is a two-step phenomenon in which the detonation pressure (shock) wave ignites a detonation product gas-air mixture. The combustion of the product gases either ignites the agent aerosol or pyrolyzes the agent. The aerosol may or may not continue to burn after the combustion of the detonation products, depending upon circumstances at the time of ignition. This concept implies that aerosol flashing can be eliminated by (a) reducing concentration or changing the composition

of the detonation product gases, (b) inhibiting the ignition and combustion of the detonation products, and (c) inhibiting the ignition and combustion of the aerosol. A successful attack on any one of these three items will break the chain of events which leads to aerosol flashing.

#### A. Influence of Detonation Product Combustion

1. Evaluation of pertinence: The working model stated that the ignition cycle could be broken by reducing the quantity or changing the composition of the detonation products.

We decided to evaluate the influence of the detonation products by performing the following experiment. A "synthetic" product gas composed of free carbon, carbon monoxide, carbon dioxide, hydrogen, water vapor, etc., would be charged into a large volume "combustion chamber", with air. A diesel fuel injector would squirt a known volume of fuel into the chamber, creating an aerosol. A spark igniter will initiate the combustion of the product gas-air mixture. The aerosol is not ignitable with a low energy spark, but the product gases are. By varying the product gas composition, aerosol particle size, and three concentration factors of product gases, air and aerosol, the following information can be obtained.

- a. The ability of the detonation products to ignite the aerosol.
- b. The ratio of product gas-air mixture to aerosol-air mixture required for ignition.
- c. Energy release required to obtain ignition and/or sustained combustion of the aerosol.
- d. The flammability limits of the combustible mixture.
- e. Relative ability of various product gas compositions to cause aerosol ignition.
- f. Effect of aerosol particle size on degree of total combustion.

Aerosol particle size was to be varied by changing the diesel fuel injector operating conditions.

2. Influence of solid detonation products: The solids produced by detonation of an explosive are primarily carbon, although in some instances nondetonated explosive particles also exist. To evaluate the effect of the detonation product gases on aerosol ignition can require inclusion of dispersed carbon particles in the synthetic gas mixtures used.

Incandescent solid carbon may itself be an ignition source. It can be conveniently studied experimentally as follows:

The combustion chamber to be used in the experiments of Section III, A-1, was to be fitted with an electrically heated "puff box." High quality carbon black is placed in this box, heated, and discharged as a solid aerosol by a puff of inert gas. The effect on the aerosol ignition can be observed as noted above. The experimental conditions to be varied would be the same as in part one above.

#### B. Shock Wave Ignition

It has been postulated that the initial factor in the ignition sequence is the shock (pressure) wave produced by detonation of the burster. This shock can ignite either a product gas-air mixture or the aerosol-air mixture directly. It is believed that a literature search and analysis will provide knowledge about the relative time history of the shock wave-agent-product gas cloud which will allow better interpretation of the significance of the shock as an ignition source.

The conditions required to achieve ignition by a shock wave can be experimentally determined in a shock tube. Three series of experiments were to be performed. The first set involves creating shocks of varying magnitude in a series of synthetic product gas-air mixtures. The second set is the same as the first except that an air aerosol and an inert gas aerosol will be used. The third set will employ a series of three-component product gas-air-aerosol mixtures.

The following information can be obtained in this type experiment:

1. Ability of shocks to cause ignition of detonation product gases and aerosols.
2. Shock energy required to achieve ignition.
3. Relative ease of igniting a product gas-air mixture and an air aerosol.
4. Influence of product gas-air mixture on ignition ease of an air aerosol.
5. Flammability limits of the two combustible mixtures separately and of the combined three component mixture.

6. Ability of a shock wave to cause direct pyrolysis of an inert gas aerosol.

7. Differences in ability to achieve sustained aerosol combustion as a function of shock energy and the presence of detonation product combustion.

8. Influence of detonation product gas composition on ease of ignition by a shock wave and ability to ignite an aerosol.

#### C. Miscellaneous Ignition Sources

Hot metal fragments and static discharges are two other possible ignition sources.

Hot metal fragments are not believed to be capable of causing aerosol ignition for two reasons: (a) they probably are not able to contact the cloud directly due to the shock wave surrounding them, and (b) they are probably beyond the cloud at the time an aerosol is capable of being ignited. Initially the agent is in direct contact with the fragments at the time of case rupture. Small jets of liquid are expelled through the initial fissures. However, this is so early in the sequence of events that even a flame from ignition of these jets would be extinguished by the aerodynamic effects of particulate movement which occurs shortly thereafter.

Some correlation exists between the material of the burster tube and occurrence of flashing, but this is not believed to be the same hot fragment ignition problem. The effect of burster tube construction material is probably related to (a) degree of explosive confinement, and/or (b) catalytic effects on the composition of the detonation product gases.

The problem can be studied experimentally by using the "puff box" technique of Section III, A-2, substituting various powdered metals for the carbon.

The ability of hot metal fragments to ignite an aerosol by the shock wave created by their high velocity can be determined by comparing shock data from experiments in Section III, B, to calculated shock energies for the fragments.

Ignition by a static discharge will be given further consideration but it is not believed that this is a cause of flashing. If the aerosol were generated by ejecting the liquid from a container via a nozzle, then it would be a probable cause. Aerosols generated by this technique can build up a charge between the cloud and the generator which can cause a "lightning flash" and aerosol ignition.

#### D. Use of Agent Combustion Inhibitors

From the agent standpoint, there is only one logical approach to the inhibition of aerosol flashing, the addition of a combustion inhibitor to the system. The combustion of an aerosol is of two types, diffusion or premixed, depending on the aerosol particle size. The actual combustion is between the vapor and air, never between the liquid and air.

The experimental approach should be:

1. Basic questions to be answered: A body of knowledge is needed on the inhibition of aerosol flashing which can be applied to the variety of problems that occur in different ammunition systems. Specifically, knowledge is required to answer the following questions:

a. What is the best inhibitor to be added to the CW agent to prevent combustion of a CW agent-air aerosol under the conditions of (1) large droplet diffusion flame, and (2) small droplet vapor-type flame, at all fuel-air ratios?

b. What is the best inhibitor to be added to the CW agent to prevent ignition of a CW agent-air aerosol when the droplets are (1) large, and (2) small, at all fuel-air ratios?

c. What is the best inhibitor which can be added to a CW agent to prevent (1) ignition, and/or (2) combustion of the detonation products of the explosive?

d. What effect does the presence of explosive detonation products have on the aerosol combustion when the products (1) do, or (2) do not burn?

2. Basic experiments to be performed: The questions require that the following be determined:

a. The ignitibility of the CW agent in air, of the detonation products in air, and of the CW agent-detonation product-air mixture as a function of the fuel-air ratio and the type of inhibitor used.

b. The combustibility (or flammability) of CW agent in air, of the detonation product in air, and of the CW agent-detonation product-air mixture, as a function of the fuel-air ratio and the type of inhibitor used.

#### E. Summary of Research Program

In summary, the following research program was planned.

1. Phase I: The factors involved in aerosol flashing are:

Particle size

Aerosol concentration

Vapor pressure

Temperature

Pressure

Flammability limits

Source of ignition

Each of these represents an experimental variable which could be investigated independently of the others. The problem is further complicated by the fact that the "source of ignition" represents a number of possible modes. This further multiplies the total number of variables to be studied, for each of the other six may be a dependent variable of the ignition source.

The ignition sources to be studied should be representative of the true situation as it exists in the field. One aim was to determine how the ignition source influences the flashing problem. A secondary benefit of this approach would be "fall out" information which would determine the most probable ignition source in explosive dissemination.

a. Variables to be studied: It was planned that in the research to be conducted we would investigate the following variables:

(1) The ability of four ignition sources to ignite aerosols, the four sources being (a) ignition by combustion of the detonation product gases, (b) ignition by shock waves with and without the presence of detonation product gases, (c) ignition by hot metal fragments, and (d) ignition by hot solid carbon particles.



(2) Aerosol particle size was to be varied. The influence of this factor on each of the four ignition sources was to be studied for nominal 5-micron and 100-micron size droplets. These sizes are representative of the two types of combustion which occur in aerosols.

(3) The effect of aerosol vapor pressure was to be studied on one or more liquids. Complete data, with variable particle size, all four ignition sources, and complete flammability limit data (as influenced by a and b above) were to be obtained on one liquid. Sufficient data were to be taken on the others to determine the influence of vapor pressure on these factors.

(4) The influence of temperature and pressure were to be confined to room temperature and atmospheric pressure. All equipment was to be designed so that other temperatures and pressures could be studied at a later time, if necessary.

(5) Flammability limit data were to be determined as a function of aerosol particle size, ignition sources, vapor pressure of liquid, aerosol-air mixture ratio, and aerosol-air-detonation product gas (three-component) mixture ratio. Construction of complete flammability limit curves would provide absolute information on the influence of aerosol concentration on ignition and combustion.

b. Experimental investigation: The experimental investigation of these variables was to be accomplished as follows. Two pieces of equipment would be used, one a special combustion chamber, and the second a shock tube. The special combustion chamber was to be a closed system with an expanding gas bag so that the pressure on the system remains constant. Aerosols would be generated with diesel fuel injectors.

Section III describes in detail both the type of experiments to be performed and the information which was to be obtained.

2. Phase II: Phase II is concerned with the use of additives to inhibit or prevent the flashing of aerosols. A series of additives were to be evaluated using a special material to represent the aerosol. This material would be similar to CW agents which are involved in the aerosol flashing problem.

Commercially available materials were to be evaluated along with some agents previously observed to have had an effect on aerosols.

The best additives were to be evaluated using both the combustion chamber and the shock tube. The flammability limit curves in which the air-aerosol-product gas mixture ratios are evaluated were to be re-evaluated using these additives to determine their effects.

#### IV. MATERIALS AND EQUIPMENT

##### A. Establishment of the Detonation Product Gas Mixture

Current devices used to disseminate liquid aerosols explosively are the 155-mm. and 8-in. artillery shells and the 115-mm. M55 rocket. Drawings of these devices were obtained from CRDL. Examination of these drawings disclosed that composition B-4 is used as a burster in all three. Composition B-4 consists of 60 per cent RDX and 40 per cent TNT, to which 0.5 per cent calcium silicate has been added. This material is vacuum cast to a loading density of about 1.72 g/cc. The explosive in the 155-mm. and 8-in. shell would be classified as under heavy confinement, according to Picatinny Arsenal. The explosive in the M55 rocket is much more lightly confined but it is difficult to assign a "degree of confinement" value to the liquid filling of this shell. Melvin A. Cook<sup>1</sup> gives a complete calculation of the detonation products produced by Composition B at a loading density of 1.58 g/cc. A partial calculation for a loading density of 1.72 g/cc shows that the total moles of gas produced are the same at the higher density. This is in contrast to the usual case where an increase in loading density results in a decrease in the total moles of gas and an increase in the free carbon content. This different effect noted with Composition B may be caused by the better oxygen balance of this explosive.

The calculated composition at 1.58 g/cc is given below.

	<u>Moles/kg</u>	<u>Per Cent by Volume</u>
CO	8.0	25.55
CO <sub>2</sub>	5.9	18.85
H <sub>2</sub>	0.01	0.032
H <sub>2</sub> O	0.1	0.32
N <sub>2</sub>	10.6	33.85
NH <sub>3</sub>	0.2	0.64
CH <sub>4</sub>	0.6	1.92
CH <sub>3</sub> OH	5.0	15.97
CH <sub>2</sub> O <sub>2</sub>	0.9	2.87
HCN	0	
C	0	
TOTAL	<u>31.3</u>	

Taking into account the facts that calculated values are subject to error because of lack of exact information regarding the correct equation of state, and Composition B is more fuel-rich than Composition B-4, it is believed that, for the purpose of this project, the above composition will serve adequately as a simulated detonation product gas mixture.

## B. Candidate Aerosol Materials

### 1. General Consideration

While the intention of the project was to obtain some basic information on the phenomenon of aerosol flashing, it was desirable that the material aerosolized have characteristics of interest to CRDL. These general characteristics are (a) a high boiling point, (b) an intermediate spontaneous ignition temperature, and (c) a high flash point. A boiling point temperature on the order of 250°C, a spontaneous ignition temperature in the 300°C range, and a flash point of 175°C were selected as meeting typical requirements.

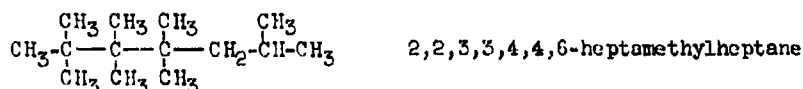
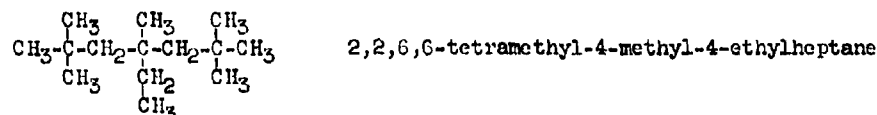
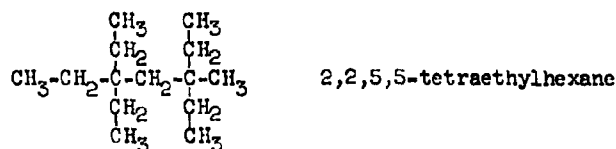
It was quickly realized that the scarcity of flash point and spontaneous ignition temperature data in these ranges would require a method of predicting values for compounds not listed in the literature. A literature search for existing data was made (covering the last 23 years) to provide the information for such predictions.

Data were obtained on four classes of compounds: pure aliphatic hydrocarbons, oxygenated hydrocarbons, aliphatic amines, and aromatic compounds.

The study made by Swartz and Orchin<sup>7/</sup> shows that the spontaneous ignition temperature value is very dependent on the surface-to-volume ratio of the equipment used to measure it. The equipment used by CRDL is believed to be similar to that used by Frank and Blackham,<sup>8/</sup> whereas most of the literature values were obtained in modifications of Bureau of Mines apparatus. By use of the information obtained by Swartz and Orchin, the value of 300°C in CRDL apparatus was graphically found to be equivalent to 262°C in Bureau-of-Mines-type apparatus.

From the work of Zabetakis et al.,<sup>9/</sup> it was found possible to predict the structure of an aliphatic hydrocarbon which would have the proper boiling point and spontaneous ignition temperature. By this method, for a spontaneous ignition temperature of 262°C, the average carbon chain length would have to be about 5.2 to 5.4 carbon atoms. For the correct boiling point, the hydrocarbon would have to contain about 14 carbon atoms.

The following type compounds fulfill these requirements:



Unfortunately none of these compounds, or anything like them, can be obtained commercially as pure materials.

The work of Zabetakis et al. clearly illustrates the two types of ignition phenomena associated with hydrocarbons. When spontaneous ignition temperature is plotted vs. average carbon chain length, a modified Z-shaped curve is obtained which shows that the short chains have ignition temperature above 400°C and the long chains below 250°C. The straight, vertical portion of the Z falls within the 250° to 400° range.

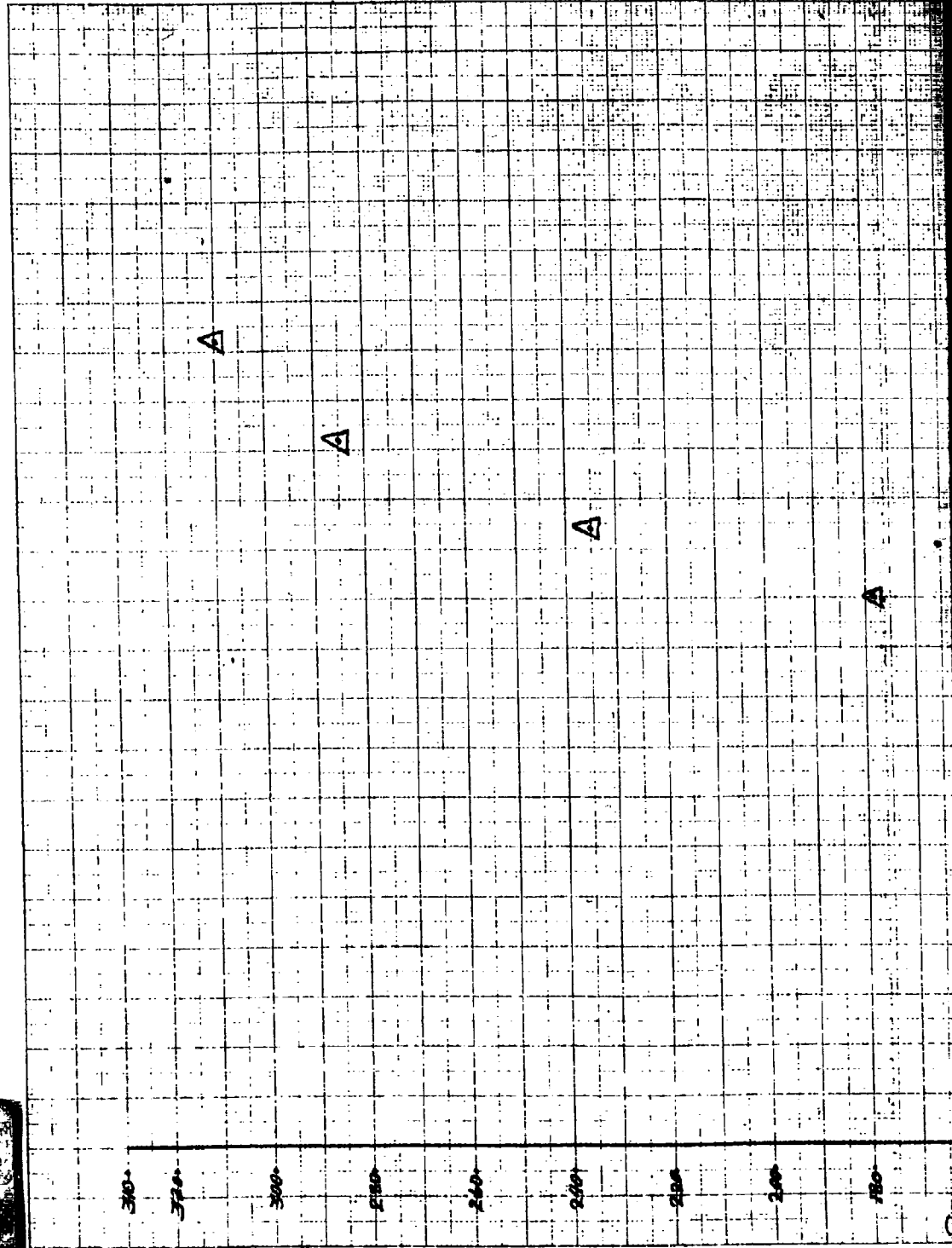
Frank and Blackham point out that additives do not change the spontaneous ignition temperature of hydrocarbons which ignite by the high-temperature mechanism. The work of Zabetakis indicates that this fact would apply to hydrocarbons whose spontaneous ignition temperature was greater than 300° to 400°C.

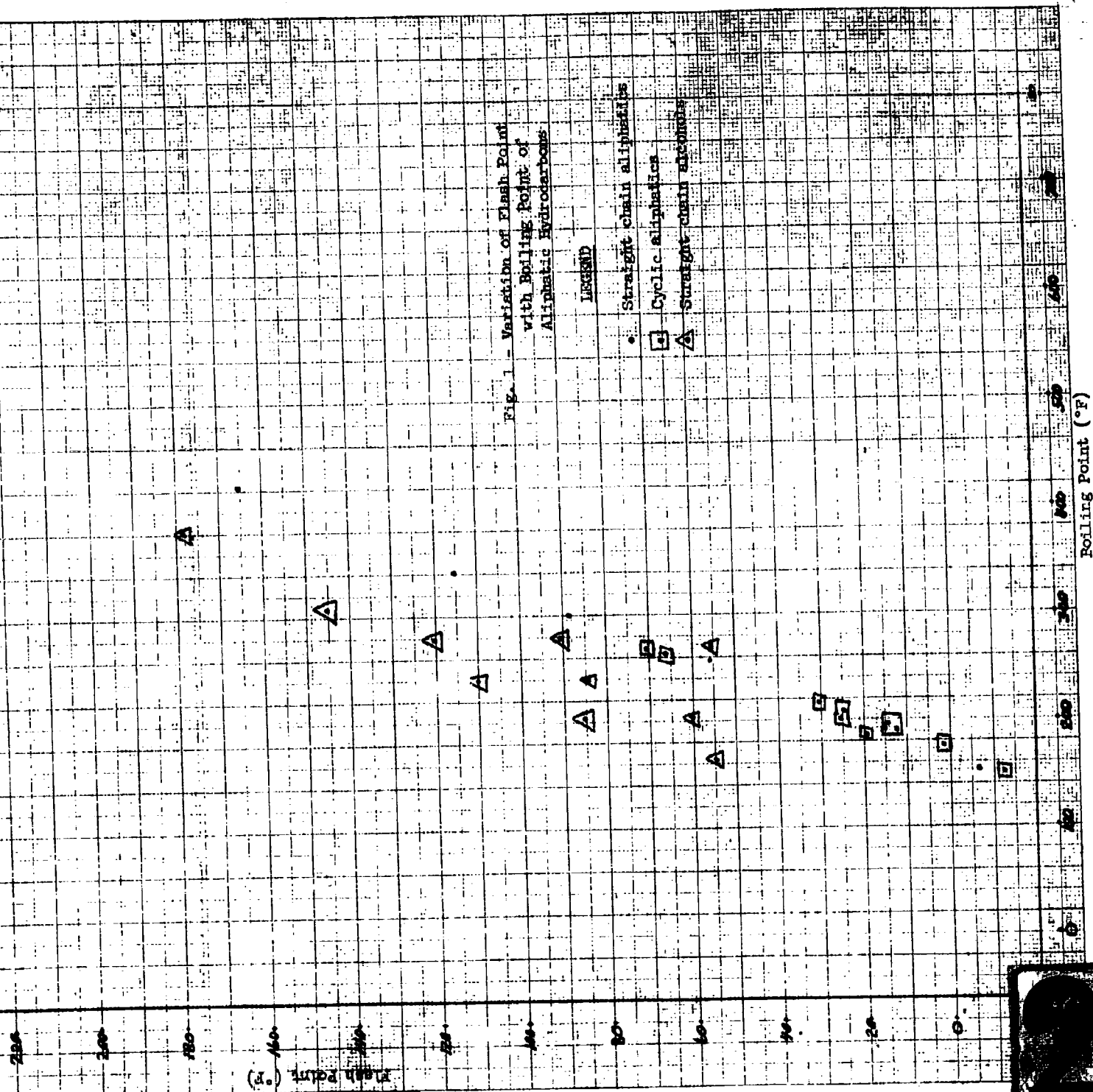
The literature data on the spontaneous ignition temperature (SIT) of oxygenated aliphatics, amines, etc., were insufficient to set up generalized rules regarding their behavior. In general, the successive substitution of OH groups on an aliphatic hydrocarbon molecule raises the SIT. The substitution of a ketone or aldehyde group lowers the SIT. The SIT values of amines are unusually high compared to corresponding hydrocarbons.

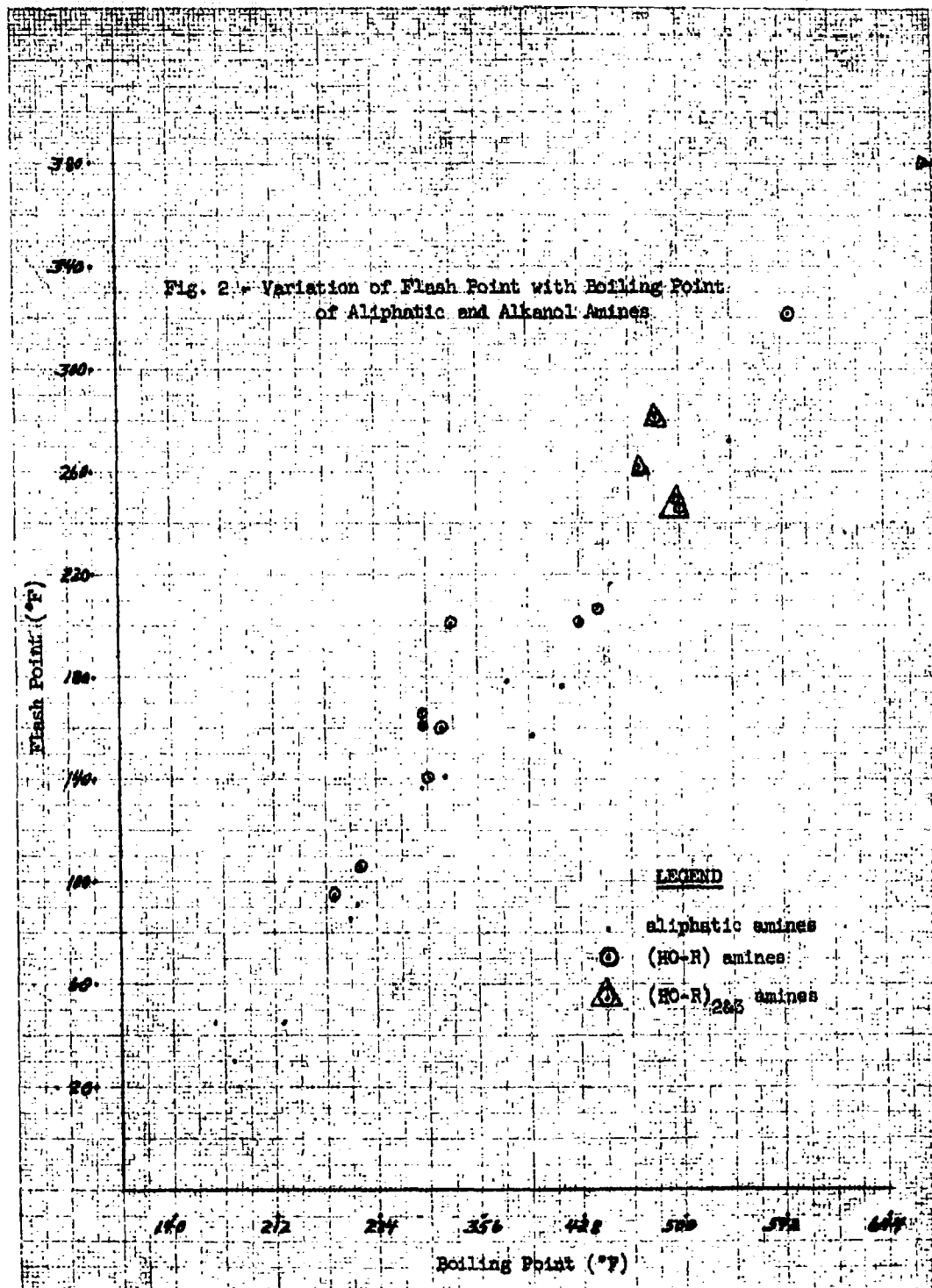
Flash point data are more readily available than SIT information. In a broad sense, flash points give a straight-line relationship with higher range boiling points for any given class of compounds. A study was made of aliphatic hydrocarbons, aliphatic alcohols and glycols, aliphatic amines, and alkanol amines. These data are given in Figs. 1 and 2.



FOR INFO ONLY 350-121







The curves indicate that in an aliphatic hydrocarbon the flash point is dependent on the boiling point. In general, it makes little difference whether or not part of the molecule is cyclic. The primary effect of an OH group is to raise the boiling point. Other than this, there is little effect, although the alcohol flash points tend to run slightly higher at a given boiling point. A large part of the scatter on both curves is believed to be due to the many sources of information used and the indiscriminate plotting of both open cup and closed cup data together, depending on which was available.

It is obvious that the proper combination of boiling point, flash point, and spontaneous ignition temperature cannot be obtained with any one of these series of compounds. It is obvious that a proper combination of boiling point and flash point alone cannot be obtained with these series of compounds.

In summary, it has been possible to find compounds which individually have the correct boiling point, or flash point, or spontaneous ignition temperature. There are some compounds which have both the proper flash point and boiling point, such as glycerin. The only compounds which are calculated to have both the correct boiling point and spontaneous ignition temperature are not available. The search for compounds which might have the desired spontaneous ignition temperature was severely hampered by lack of published data.

A search of chemical warfare agents disclosed that compound QL comes close to the desired properties and is of low toxicity. This compound was proposed as a test material and was accepted. The spontaneous ignition temperature of QL is high. Other materials to be evaluated will have to be selected with the thought of achieving a close match in spontaneous ignition temperature.

2. Use of QL aerosols: It was originally planned that the bulk of the experimental work would be accomplished with glycerin as a test material. Glycerin was selected as being representative of a number of properties which seemed desirable to investigate. Subsequent to initiation of the contract it was mutually agreed that the range of properties should be changed. This caused the initiation of a search for a suitable material, which is described above. As a result of the search, the CRDL compound that is coded QL, was selected as a suitable compromise for the factors to be studied. The use of QL has caused some unplanned-for problems and these are discussed below.

While QL is of low toxicity, it has a toxic potential. It reacts with oxygen and water. It is incompatible with rubber and plastics except Teflon. It can decompose in storage with an increase in container pressure. The toxicity and potential toxicity of QL require that due care must be exercised because of the potential hazard.



The reactivity of QL with water and oxygen requires that it be protected from the atmosphere at all times. This means that all equipment into which it is introduced must be dried and flushed if it is to remain pure for any length of time. Opening a system which contains it must be done under dry nitrogen, and then the container must be resealed under dry nitrogen. All equipment must be designed and built with this factor in mind.

The incompatibility of QL with rubber and plastics has caused a number of problems. All equipment must be designed to use Teflon gaskets and seals. This seems rather insignificant until it is realized that Teflon is a very poor substitute for an elastomer. Consequently, it is difficult to obtain a dynamic seal with it. Static seals are almost impossible with "O" rings because of Teflon's extreme cold flow tendency. However, in a number of instances we have been forced into using Teflon "O" rings for static seals.

QL is not compatible with Silastic either, but we had to use RTV Silastic for gaskets between the end plates and plastic wall of the combustion chamber. It was originally designed and built for rubber "O" rings. A substitution of Teflon "O" rings did not work at all and a seal was not obtainable. Neither could we obtain a seal with a flat Teflon gasket. The plastic surface was just uneven enough and the strength of threads in the chamber wall was just weak enough, so that we could not bring enough pressure to bear to achieve a seal with Teflon sheet. Consequently, we constructed a mold and made two RTV Silastic gaskets. So far these are working out well.

The injection pump we were to use to create aerosols was designed by the manufacturer to use rubber "O" rings. We have substituted Teflon. Just obtaining correct sizes for substitution has been a problem because there seems to be a lack of correspondence in "O" ring sizes between these materials. Two of these "O" rings are very critical and both are dynamic seals. One is on the piston assembly and the other is in the check valve assembly. In fact, this latter "O" ring is the check valve. Some difficulty has already been experienced in proper pump operation.

All seals in the shock tube have been designed for use with Teflon.

The tendency of QL to decompose in storage with an increase in container pressure has resulted in one accident to date. Ampoules containing 400 ml. of QL were received from CRDL. The first one opened was observed to be under a positive pressure and had a pungent, penetrating smell. On the assumption that this was normal, the ampoule was connected on to the aerosol generation system. A nitrogen bleed was started to purge the pump overnight. The following morning Mr. Pollock examined the setup, and arrived just in time to be thoroughly sprayed by QL leaking past the plastic connection of the ampoule on the system. Later reconstruction of the events led to the conclusion that

gas pressure inside the ampoule had forced the ampoule out of the connection and sprayed the material. It was bad luck that Mr. Pollock arrived just at that moment. All 400 ml. were sprayed out all over the room and equipment. Thorough decontamination of the room and equipment followed. Mr. Pollock suffered no apparent lasting ill effects from the exposure.

The accident convinced us that this must not be normal QL behavior and that the material had decomposed in storage. Because of our experience with this sample, we decided to vacuum distill the next ampoule and assay its purity.

Two documents, CRDL Technical Memorandum No. 14-15 titled, "Gas Chromatography of BZ, VX, QL, and GE," and Food Machinery and Chemical Corporation Final Report on Contract DA-11-032-ENG-7295, dated August 1961, were consulted to determine previous experience in this area.

To accomplish the distillation, we used a vacuum jacketed glass column 1 in. I.D. x 4 ft. long, packed with glass helices. A Corad constant ratio distilling head gave us a reflux ratio of about one to one. The system was operated at 1 mm. mercury pressure with a continuous nitrogen sweep through the column, head, and receiver. To assay the sample, we used a Micro-Tek, Model GC-2500R programmed temperature gas chromatograph.

Knowing that QL is compatible with Apiezon grease, the distillation system was assembled from standard fittings and stopcocks, using Apiezon N grease for vacuum sealing. This was an error, because QL vapor and liquid are such excellent solvents for Apiezon grease. Any future distillation should be conducted in apparatus with Teflon fittings.

We were surprised when we opened the second ampoule in preparation for filling the distillation flask. There appeared to be no pressure in the ampoule, and it was comparatively free of strong odor. We took a sample of this for chromatographic analysis, and proceeded with the distillation. The distilled material was separated into three fractions, 75 ml. in the first fraction which was discarded, 275 ml. in the second which was retained, and 50 ml. left in the pot.

Problems were encountered in making quantitative assays of QL. Gas chromatograph columns prepared by the method in the cited references do not produce a column with a known amount of stationary phase. Consequently, the column time constants and curve area relationship for previously reported columns cannot be used. Lacking a known sample of any material or constituent to calibrate our column, a request for a "known" was made to CRDL. The distillation procedure should produce some reasonably purified material and we elected

to use this as a qualitative reference standard. We have since received a pure sample of TR which will be a significant aid in calibrating our columns and correlating with the published data.

The chromatograph of the original material and of each of the three fractions indicated that the distillation increased the height of the QL peak but that all of the samples were very similar. The distillation primarily reduced the percentage of high boiling impurities.

In view of the marked difference between these first two ampoules (i.e., internal pressure and odor), and lack of a major improvement in purity of the second ampoule on distillation, we have decided not to distill future ampoules unless they exhibit strong odor or pressure. None of the ampoules opened subsequently have shown signs of deterioration.

We have noted that there are several physiological effects on personnel using QL. Exposure to the vapor can bring on stomach upset and difficulty in breathing (described as a "tightness in the lungs"). Skin dermatitis has been noted in the form of an itchy red rash which covers large areas of the body. The dermatitis condition can occur from vapor exposure alone. The intestinal and lung disturbance clears up in a few hours; the dermatitis in a few days, following exposure.

#### C. Combustion Chamber Design and Fabrication

A combustion chamber to evaluate a number of the parameters involved in aerosol flashing was designed and fabricated. The general specifications for the apparatus were as follows:

1. It must allow the creation of any desired combustible component mixture composition in a three-component system.
2. It must allow the combustion to be studied under constant pressure conditions.
3. It must be a totally closed system to permit recovery of combustion products as desired.

To achieve these specifications the concept of a long cylindrical chamber, separated from a collapsed, flexible bag by a rupture diaphragm was adopted.

The combustion chamber can be divided into a number of subassemblies which are discussed individually below.

1. Main chamber: Photographs of the equipment are presented in Figs. 3 and 4. The main chamber consists of a 36-in. long by nominal 5-1/2-in. I.D., clear plastic cylinder, set vertically in a stand. The system volume is 13.9 liters. On a metal plate at the bottom (not shown) is mounted a diesel fuel injector for dispersing the liquid phase material. The bottom plate also has a provision for spray washing the interior, evacuating, and draining. A metal collar at the top of the cylinder contains a perforated plate, igniter access, connections for a gas expansion bag, and a spray nozzle for bag washing.

The perforated plate is a support for the rupture diaphragm and consists of 13/64-in. holes on 1/4-in. staggered centers. The plate's open area is 60 per cent. Testing of several diaphragm materials (including several types of aluminum foil) led to the selection of Saran wrap as the most desirable. It is cheap, readily available, and uniform in characteristics. When supported by the perforated plate, it will withstand a pressure differential greater than 20 psi. When unsupported as a 5-1/2-in. diameter diaphragm, it breaks at less than 1 psi pressure differential.

When the chamber is evacuated for filling with the combustible mixture, the perforated plate supports the rupture diaphragm, seals the system from the atmosphere, and prevents a combustible mixture from entering the expansion bag. When the mixture is ignited, the increased pressure in the chamber pushes the diaphragm away from the plate. Since it is unsupported across the 5-1/2-in. diameter of the tube, it ruptures at a very low pressure. Due to the large open area of the support plate, the expanding gas experiences no significant impediment to its flow into the bag.

The bag is designed to contain all of the volume increase caused by burning of the combustibles. It is constructed of polyvinyl sheet, heat-sealed to form an air-tight bag. Provision has been made to flush the bag with nitrogen gas.

Because of the nature of the materials to be studied, it was desirable to eliminate all rubber "O" rings and gaskets in the system. Gaskets between the Plexiglas tube and aluminum attachments were cast from Silastic RTV Silicone Rubber.

A spark igniter has been fabricated. The circuit is basically that of a capacitor bank fired on command by a 5C22 hydrogen thyratron tube. Pointed, 1/8-in. diameter tungsten rods are used as spark electrodes. The output is variable up to 160 joules maximum.

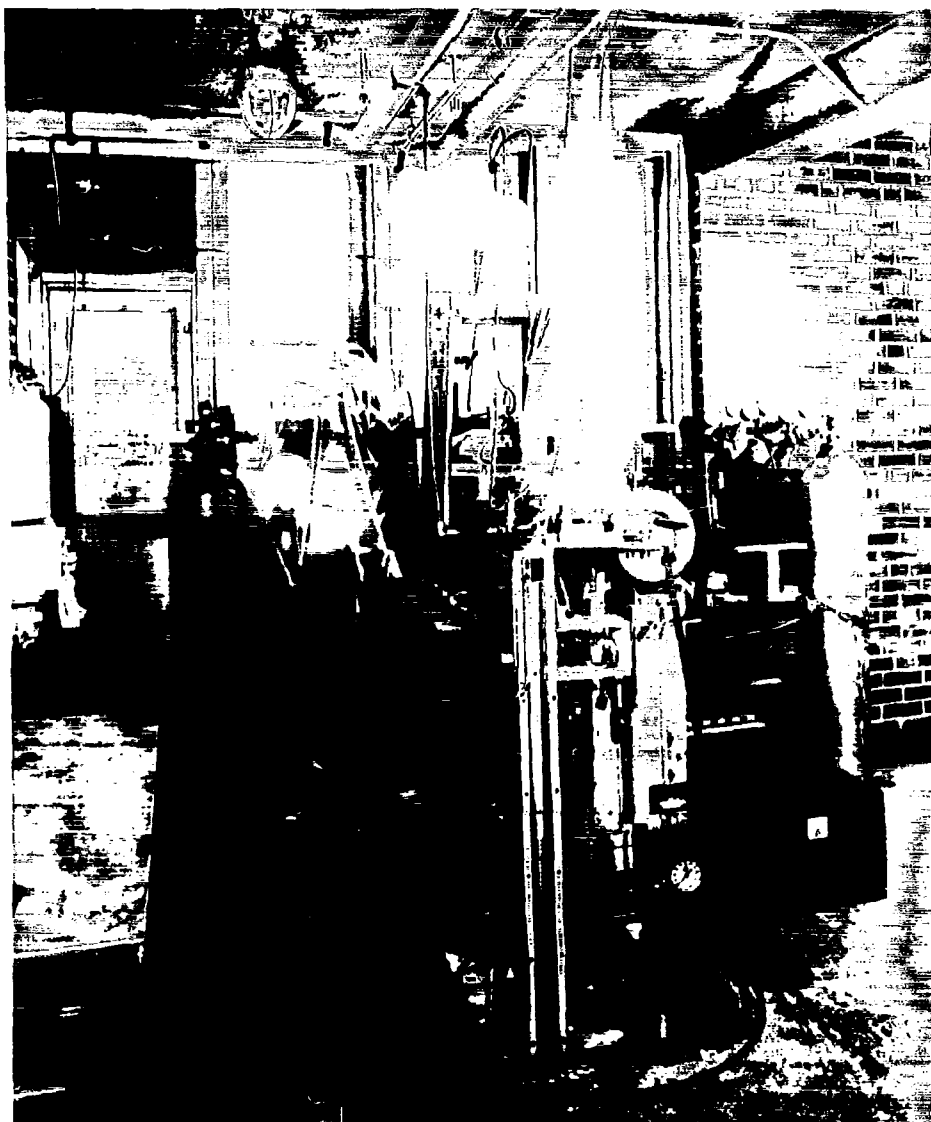


Fig. 3 - Over-All View of Combustion Chamber Showing All  
Accessory Equipment and Facilities

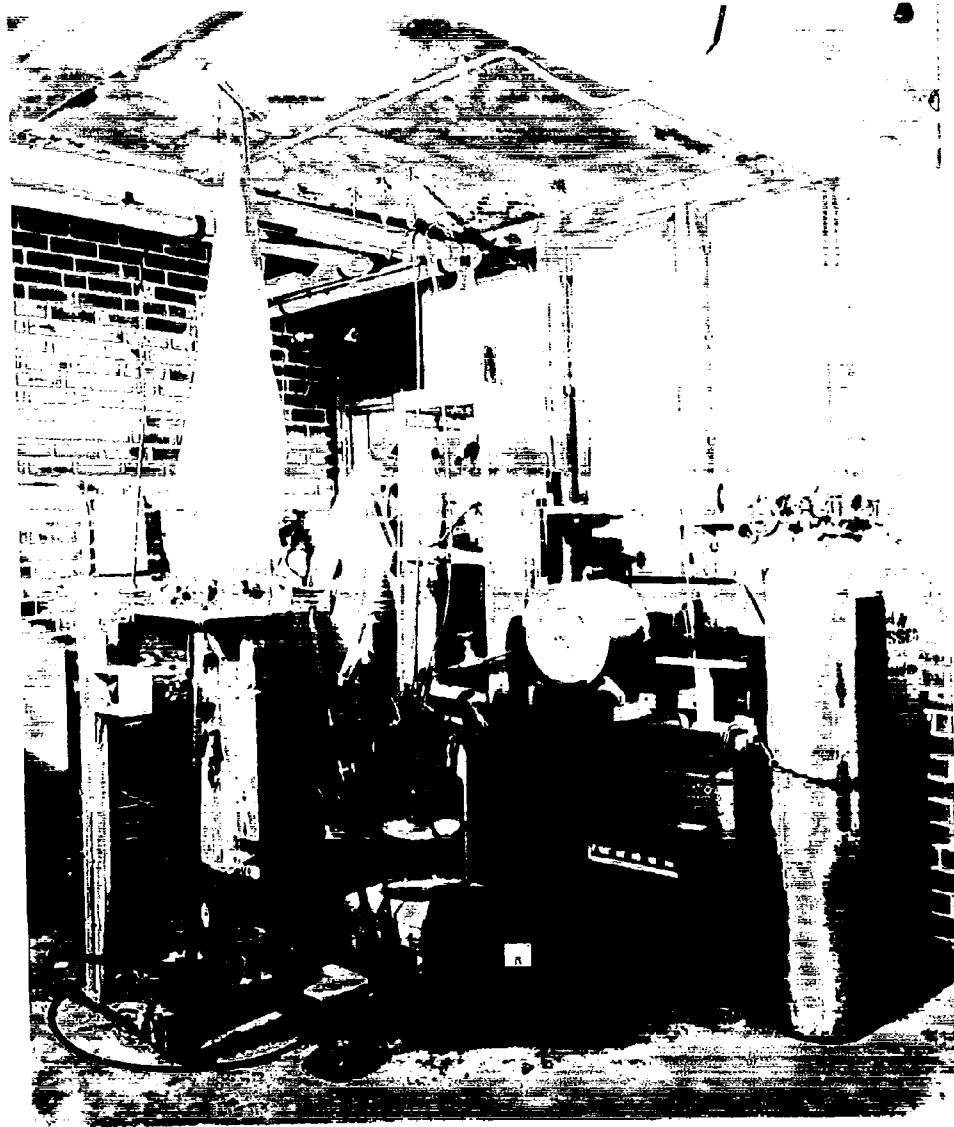


Fig. 4 - Over-All View of Combustion Chamber Showing All  
Accessory Equipment and Facilities

2. Aerosol injection system: The aerosol injection system must be protected from the atmosphere since QL reacts with both oxygen and water. In addition, it is necessary that means be provided to determine how much liquid is aerosolized in each experimental run. Further, the pump is a positive displacement type and requires a head of at least 15 psia to fill the pump chamber on each stroke. All of these features are incorporated in the assembly shown in Fig. 5.

The QL is received in sealed ampoules containing about 400 ml. of material. Such an ampoule is shown at the top in Fig. 5. This is joined by a Teflon sleeve to the balance of the filling system. The filling system consists of two parts, a storage area and a burette. The storage area is separated from the burette by two stopcocks. Essentially, the entire assembly is just a standard burette filling system with provision for replenishing the atmosphere above the stored liquid with dry nitrogen gas rather than having it open to the atmosphere. The lower Teflon stopcock selectively opens the storage area to fill the burette, or connects the burette to the pump. At the top of the burette are three stopcocks. The one on the right opens the system to a nitrogen cylinder to bleed nitrogen gas into the system. The one directly above the burette (almost hidden in Fig. 5) opens the system to the atmosphere through a tiny hole about 1/2 mm. diameter. This allows a continuous nitrogen flush in the system and breaks the "pump vacuum" so that the aerosol injector pump chamber will fill. The third stopcock (the one on the left in Fig. 5) allows nitrogen gas to pass into the storage bulb so that the burette will fill. A close examination of Fig. 5 will disclose a breather tube which extends from the storage area inlet nitrogen lineup into the storage ampoule. This permits the nitrogen gas to pass directly into the open volume above the liquid. More importantly, this breather tube allows excess pressure that can build up in the storage area to be vented to the atmosphere.

The filling system is connected to the pump via a glass-to-stainless-steel ball and socket joint as shown. The stainless-steel socket terminates in a special pump adapter which can be seen in Fig. 4. A Teflon "O" ring between the adapter and pump seals this inlet line.

The quantity of liquid delivered can be controlled by the piston displacement in the pump, i.e., by the length of stroke of the pump handle. By using various sizes of drill rod stock as blocks between the pump housing and the handle, the quantity of liquid delivered at any pressure can be controlled to within  $\pm 0.005$  ml. In the volume of the test equipment, the flammability range was predicted to be between 1 to 4 ml. of material, so this accuracy of delivery was quite adequate. However, a check was inserted in the system to insure that the "dead-reckoned" quantity was actually delivered. This is the reason for the burette.

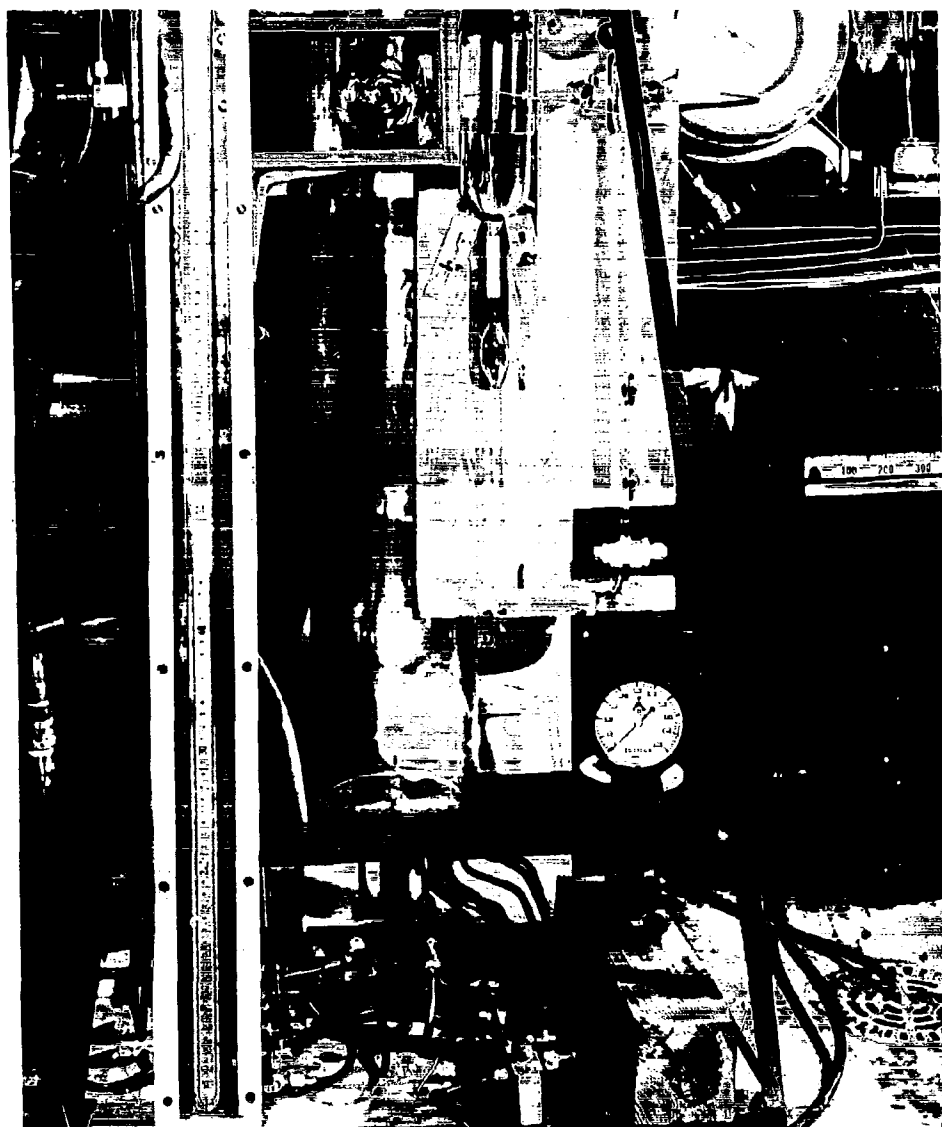


Fig. 5 - Aerosol Injection System Showing Method of Isolating QL  
from Atmosphere



The system was "activated" by opening the QL ampoule under a nitrogen blanket in a sealed plastic bag and assembling it to the storage part of the system which was also contained in the bag. The oven-dried glass parts were flushed with nitrogen for a day prior to introducing the QL ampoule. With the ampoule attached, the filling system was attached to the pump. By flowing nitrogen through the burette, the pump and injector nozzle are thoroughly flushed before admitting QL into the burette.

3. Detonation product gas: The CO, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> components of the detonation product gas mixture were supplied as a mixed gas by Matheson but they could not add in the components to form the complete mix. To enable us to work with the original gas mixture as planned, we have made up a simple system to form the complete mix in the chamber.

A stock solution of the liquid components was prepared in proportions equivalent to those found in the detonation product gas mixture. An arrangement was made whereby a hypodermic syringe is attached to the stock solution bottle which enables us to withdraw known measured quantities. A similar adapter for the hypodermic syringe is attached to a "flasher" chamber. The "flasher" chamber is merely a glass bottle set on a hot plate. The stopper contains the hypodermic syringe adapter and has a gas entrance and exit line. The entrance line is from the cylinder containing the five-component gas mix. The exit line leads to the combustion chamber. The liquid solution is injected into the warmed chamber where the Matheson gas mixture evaporates it, and carries it into the combustion chamber. Mixing is accomplished in the combustion chamber. Of course, the amount of solution injected is in proportion to the quantity of five-component Matheson gas which is being used. The liquid components will remain in the vapor phase at room temperature. All lines in this portion of the system are stainless steel. A flow schematic of this system is included in Fig. 6. A "flasher" chamber can be seen between the Wet Test Meter and the gas cylinders on the table in Fig. 4. Immediately behind the hypodermic syringe sticking above the flasher in Fig. 5 is the bottle containing the liquid stock solution.

4. Ignition system: The igniter is basically a capacitor bank fired on command by a 5C22 hydrogen thyratron tube. Pointed, 1/8-in. diameter tungsten rods are used as spark electrodes. A circuit diagram of this unit is presented in Fig. 7. The output is variable up to 175 joules maximum. The system is shown at the lower center of Fig. 4.

It turns out that the output is not really as variable as was originally planned. The system is designed to vary the output by varying the voltage at constant capacitance, since the output in joules is equal to  $1/2 CV^2$  where C is the capacitance and V is the voltage. However, it is desirable to keep the spark gap constant at about 0.1 in. If the ignition system output is varied as

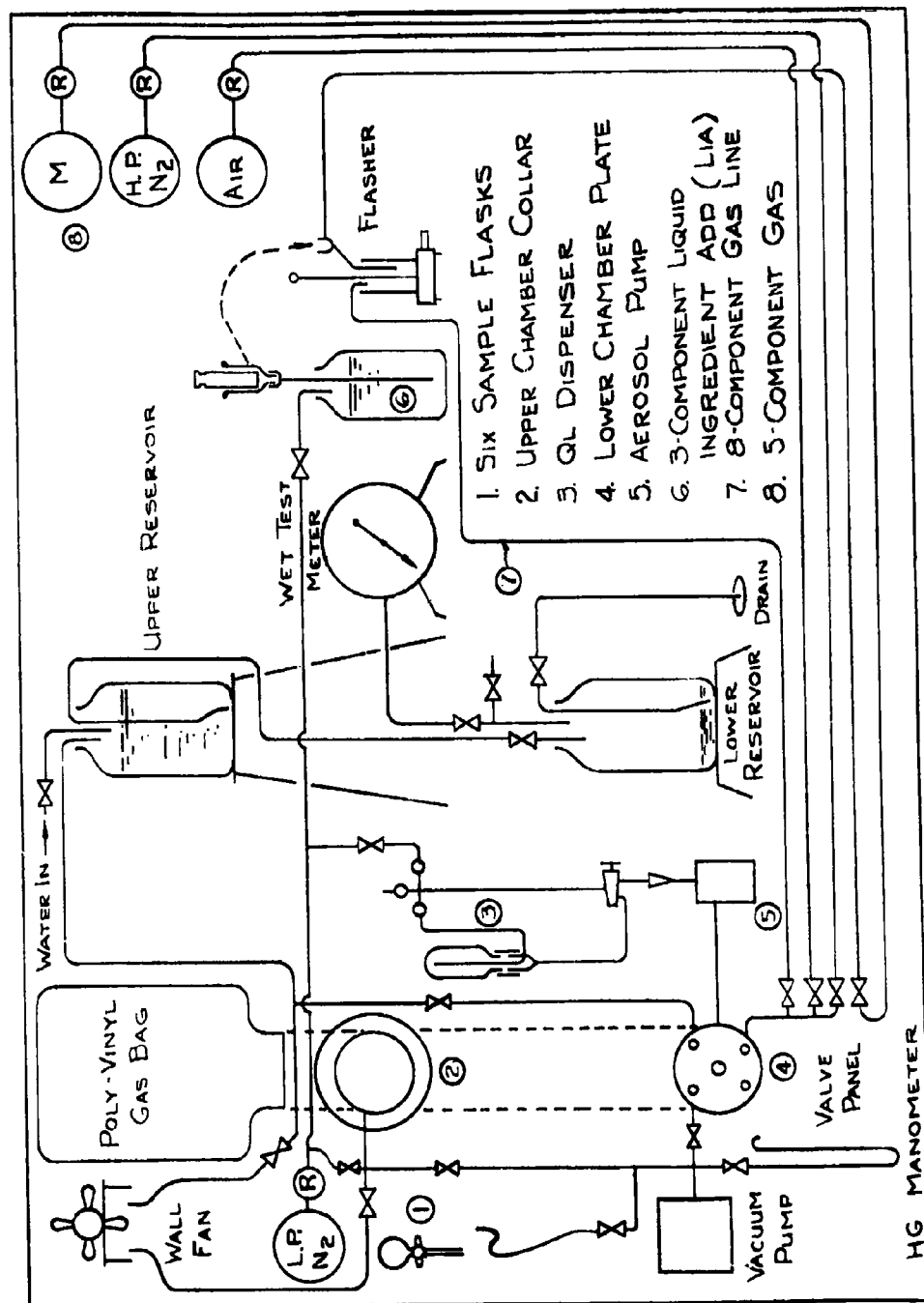


Fig. 6 - Schematic of Combustion Chamber System Showing Gas Lines



a function of voltage, the spark gap has to be continuously readjusted in order to get a current flow in the system because the maximum voltage available (5,000 v.) is the voltage required to break down on a 0.1 in. spark gap. Since two of mfd capacitors are used to obtain the maximum output, we elected to perform the studies using one capacitor at 5,000 v. at 0.1 in. electrode spacing in all tests. This gives us about 83 joules ignition energy which is more than adequate.

5. Gas sampling system: It had been planned to sample the gas after combustion to determine the proportion of aerosol consumed. It was originally planned that the system would be washed with a water spray to collect a glycerine aerosol. With the change to QL, we elected to attempt gas sampling rather than trying to wash the system. Consequently, based on the assumed sensitivity of gas chromatography to QL, we decided to take a 200-ml. gas sample. If all of the QL in a 200-ml. sample is dissolved into 10 ml. of benzene, the chromatograph should be able to detect 1 per cent of the quantity of QL required to form what we believe might be equivalent to the fuel lean limit mixture.

The sample bulb rack is shown at the left of the combustion chamber stand in Fig. 3. The sample bulbs are 200 ml. flasks with stopcock attached. The long shank on the bulb goes through a bushing in the chamber wall as shown as the left center in Fig. 4. A sample bulb in position is shown in both Figs. 3 and 4. The wood frame around the bulb is to protect it and keep it from being accidentally broken. The bulbs are evacuated before use.

Since we changed to a gas sampling procedure, it was necessary to know the total volume of gas after the combustion reaction in order to be able to calculate the quantity of unconsumed QL. Any increase in volume is captured by the plastic bag. Therefore, if the quantity of gas in the bag were measured after an experiment, the total gas volume could be obtained. Measurement of this gas volume is the purpose of the two water jugs and the Wet Test Meter shown in Figs. 3 and 4. The flow diagram is given in Fig. 6. Basically it works as follows: The introduction of the combustion gas directly into the meter is undesirable because of its corrosive and possible toxic nature. Therefore, it is separated from the meter by the two jugs. The elevated jug is filled with water and the lower jug of Fig. 4 is filled with air. When a syphon is started between the two jugs, gas is pulled (pumped) out of the chamber to replace the lost volume. As the water level rises in the lower jug, clean air is forced through the Wet Test Meter. Since there is a one-to-one correspondence between the chamber combustion gas and the clean air measured by the Wet Test Meter via the water displaced, we have a very simple, clean, self-pumping, gas measuring system.

#### D. Shock Tube Design and Fabrication

Calculations were made to determine the operating parameters of a shock tube which will achieve the temperature pulses predicted to ignite the aerosol-product gas mixtures. The physical design of the tube is based on these calculations.

The analysis described herein is applicable to conventional shock tubes which provide high temperature regions behind reflected shock waves at the closed end of the "receiver" section. The reflected expansion wave from the closed end of the "driver" section is returned to the "receiver" end and terminates the high temperature operation after a predictable time interval.

Figure 8 illustrates a travel time diagram of the shock tube operating characteristics.

The incident shock wave A, traveling along the tube at  $W_A$ , is generated when the diaphragm is ruptured. The bursting of the diaphragm also generates a centered expansion wave which moves to the left into the high pressure driver gas. The "contact surface" is the interface between the driver gas and the receiver gas and moves at a velocity equal to  $U_2$ . The shock wave B reflected from the closed end of the receiver generates a high-pressure, high-temperature region. The interaction of the reflected shock wave B with the contact surface will, in general, produce reflected shock waves which will subject the test section gases to a series of temperature steps. Since this is considered to be undesirable, it was decided to return the reflected expansion wave head at a point in time and space coincident with or below the coincidence point m formed by the intersection of the reflected shock B and the contact surface. This requirement therefore specifies a minimum length  $L_R$  (receiver section) for a given  $L_d$  length (driver section).

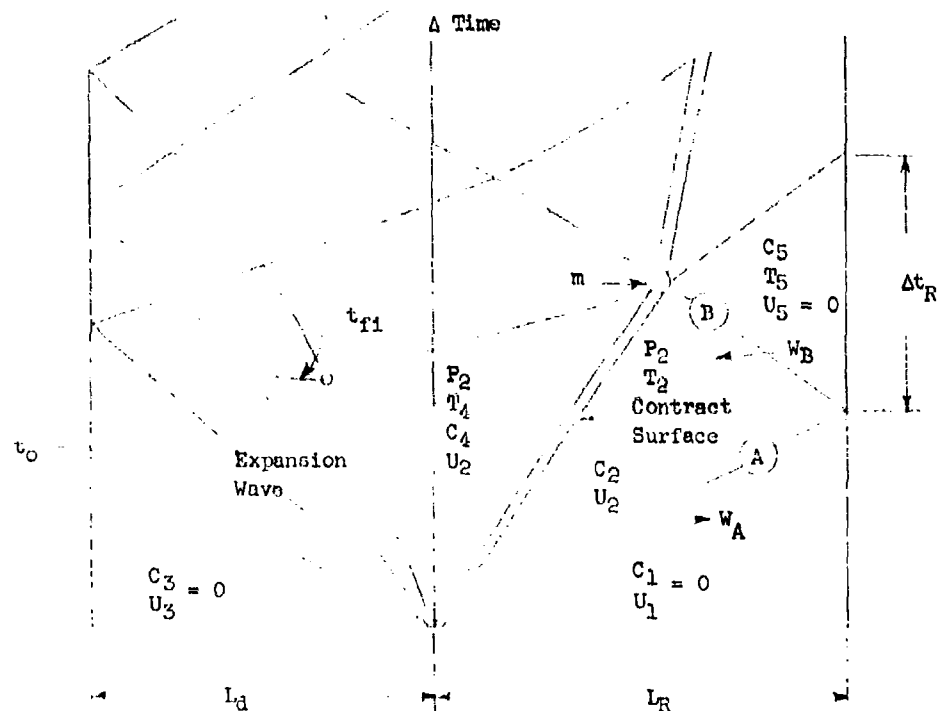


Fig. 8 - A Shock Wave Time-Travel Diagram

The intensities of the properties in the various regions can be quite simply determined from the shock wave and expansion wave relationships and the thermodynamic properties of the gases involved. The following is a listing of significant shock tube relationships derived for a receiver gas with an assumed specific heat ratio ( $k$ ) of 1.35:

$$\frac{P_2}{P_1} = \frac{2kM_{xA}^2(k-1)}{k+1} = \frac{7.72M_{xA}^2-1}{6.72} \quad (1)$$

$$\frac{T_2}{T_1} = \frac{\left(\frac{P_2}{P_1}\right) [(k-1)M_{xA}^2 + 2]}{(k+1)M_{xA}^2} = \frac{\left(\frac{P_2}{P_1}\right) [M_{xA}^2 + 5.72]}{6.72M_{xA}^2} \quad (2)$$

$$\frac{C_2}{C_1} = \sqrt{\frac{T_2}{T_1}} \quad (3)$$

$$\phi = \frac{M_{xA}^2}{M_{xA} \left(\frac{C_2}{C_1}\right)} \quad (W_A = M_{xA} C_1) \quad (4)$$

$$M_{xB} = \frac{\phi + \sqrt{\phi^2 + 4}}{2} \quad (W_B = U_2 - M_{xB} C_2) \quad (5)$$

$$\frac{P_5}{P_2} = \frac{2kM_{xB}^2 - (k-1)}{k+1} = \frac{7.72M_{xB}^2 - 1}{6.72} \quad (6)$$

$$\frac{T_5}{T_2} = \frac{\left(\frac{P_5}{P_2}\right) [(k-1)M_{xB}^2 + 2]}{(k+1)M_{xB}^2} = \frac{\left(\frac{P_5}{P_2}\right) [M_{xB}^2 + 5.72]}{6.72M_{xB}^2} \quad (7)$$

$$\frac{C_5}{C_2} = \sqrt{\frac{T_5}{T_2}} \quad (8)$$

$$\frac{U_2}{C_1} = \frac{2}{k+1} \left( \frac{M_{xA}^2}{M_{xA}} \right) = 0.85 \left( \frac{M_{xA}^2}{M_{xA}} \right) \quad (9)$$

$$\frac{t_o}{t_{f1}} = \left[ 1 - \frac{k_d - 1}{2} \left( \frac{U_2}{C_3} \right) \right] \frac{k_d + 1}{2(k_d - 1)} = \left[ 1 - 0.33 \frac{U_2}{C_1} \right]^{2.02} \quad \begin{array}{l} \text{(For Helium Driver} \\ \text{at Atmos. Temp.)} \\ (k_d = 1.66) \end{array} \quad (10)$$

$$\frac{t_o}{t_{f1}} = \left[ 1 - 0.2 \frac{U_2}{C_1} \right]^3 \quad \begin{array}{l} \text{(For Nitrogen Driver} \\ \text{at Atmos. Temp.)} \\ (k_d = 1.40) \end{array} \quad (11)$$

$$\left( \frac{P_2}{P_3} \right)_{\text{He}} = \left[ 1 - 0.096 \left( \frac{M_{xA}^2}{M_{xA}} \right) \right]^{5.02} \quad \text{(For Helium Driver Gas)} \quad (12)$$

$$\left( \frac{P_2}{P_3} \right)_{\text{N}_2} = \left[ 1 - 0.167 \left( \frac{M_{xA}^2}{M_{xA}} \right) \right]^7 \quad \text{(For Nitrogen Driver Gas)} \quad (13)$$

The derivation of operating time ( $\Delta t_R$ ) as a function of the tube lengths  $L_R$  and  $L_d$  resulted in the following equation:

$$\frac{\Delta t_R C_3}{L_d} = K_1 \left\{ 1 - K_2 \left( \frac{L_R}{L_d} \right) \right\} \quad (14)$$

where

$$K_1 = \frac{2 \left( M_{xB} + \frac{C_5}{C_2} - \frac{U_2}{C_2} \right)}{(1 + M_{xB}) \left( \frac{t_o}{t_{f1}} \right) \left( \frac{C_5}{C_2} \right)} \quad (15)$$



and

$$K_2 = \frac{1}{2} \left( \frac{t_o}{t_{f1}} \right) \left( \frac{c_3}{c_2} \right) \left[ \frac{\left( \frac{u_2}{c_1} + \frac{c_2}{c_1} \right)}{M_{xA}} - 1 \right] \quad (16)$$

The calculated values for the significant variables are given in graphical form in Figs. 9 through 12.

Figure 9 presents significant shock tube pressure ratios and temperature ratios versus the incident shock wave Mach number ( $M_{xA}$ ) as derived from Eqs. (1) through (13). Initial driver pressure ( $P_3$ ) to develop a specified test chamber temperature pulse magnitude ( $T_5$ ), as well as test chamber pressure magnitude ( $P_5$ ) can be determined from this chart.

Figures 10 and 11 present the functions  $K_1$  and  $K_2$  for helium and nitrogen gas drivers for use in Eq. (14) and define operating times as a function of driver length ( $L_d$ ) and receiver length ( $L_R$ ).

Figure 12 presents minimum ( $L_R/L_d$ ) ratios for nitrogen and helium gas drivers as a function of  $M_{xA}$ . These values have been derived from the following relationship which specifies the ( $L_R/L_d$ ) value which will achieve intersection of the reflected expansion wave leading edge with the contact surface-reflected shock wave coincidence:

$$\left( \frac{L_R}{L_d} \right)_{\min.} = \frac{2M_{xA} M_{xB} \left( \frac{c_2}{c_1} \right)}{\left( \frac{c_3}{c_1} \right) \left( \frac{t_o}{t_{f1}} \right) \left[ \left( \frac{c_2}{c_1} \right) M_{xB} + M_{xA} - \frac{u_2}{c_1} \right]} \quad (17)$$

The design of the shock tube facility was based on these calculations. Mach 4.25 was selected as the upper shock level for consideration inasmuch as this will heat the aerosol mixture to about 2000°C. This was predicted to be more than sufficient to achieve ignition.

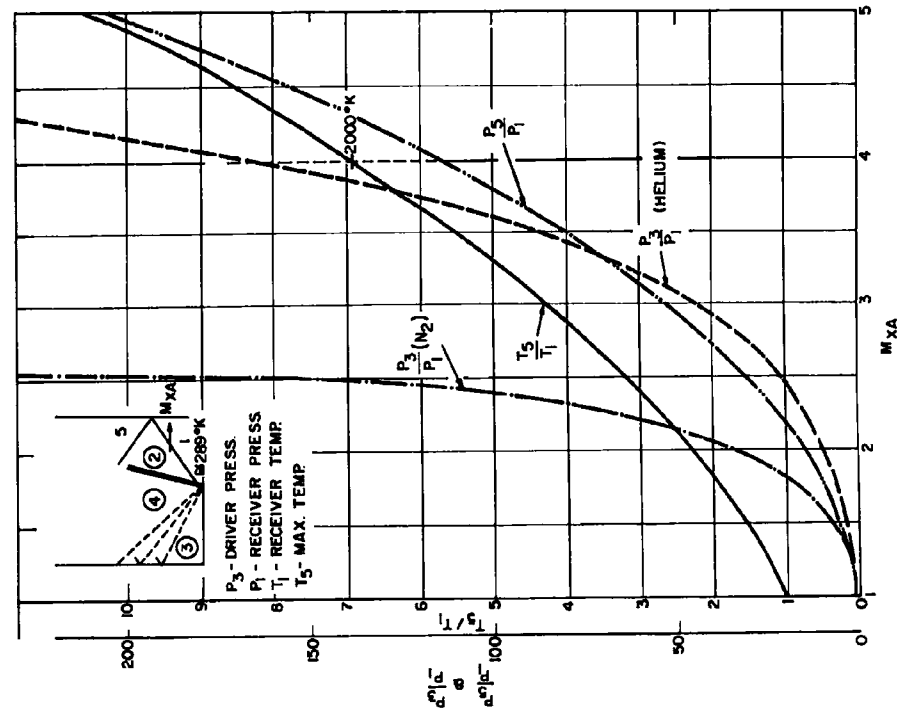


Fig. 9 - Shock Tube Pressure and Temperature Ratios vs. Incident Shock Wave Mach Number

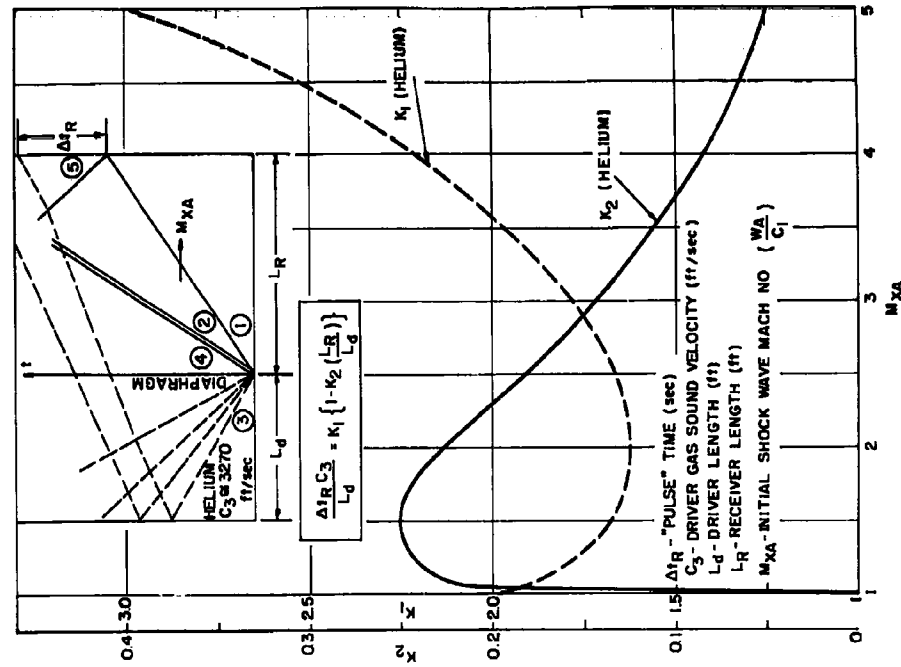


Fig. 10 - Constants for Evaluation of "Pulse" Times for Helium Driver Gas

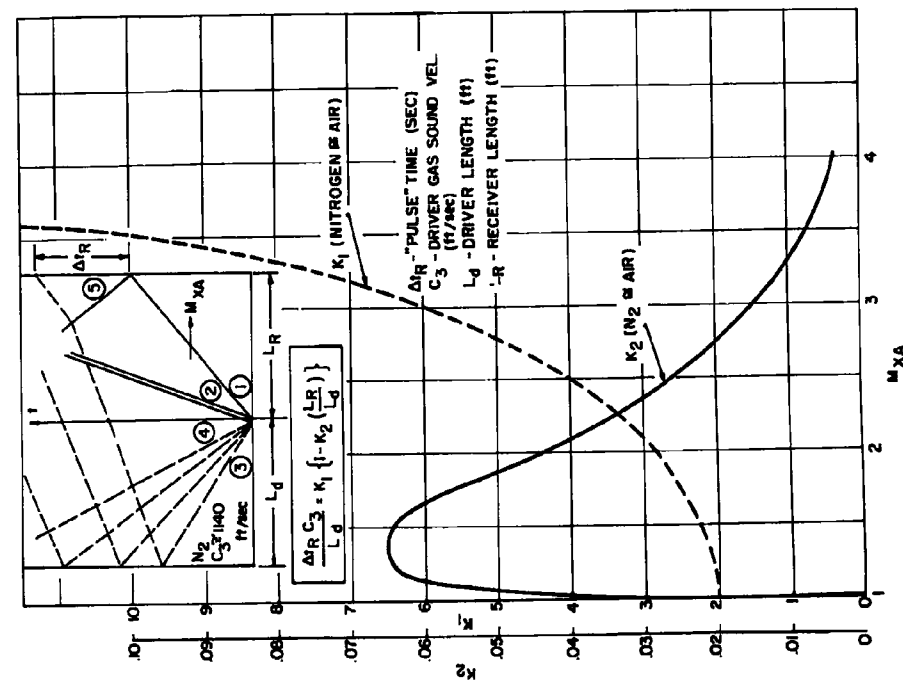


Fig. 11 - Constants for Evaluation of "Pulse" Times for Nitrogen Driver Gas

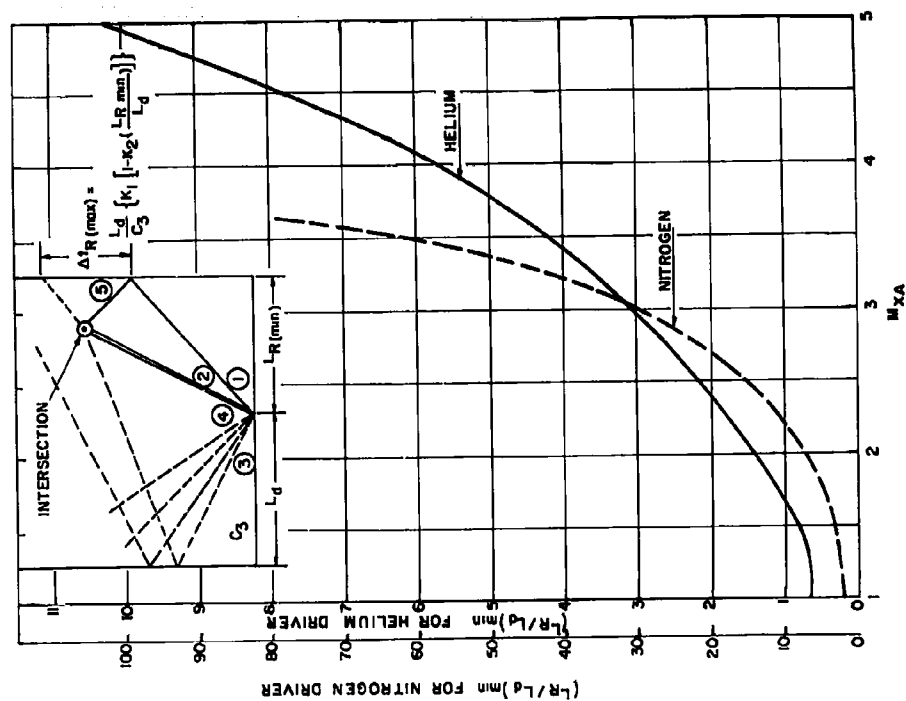


Fig. 12 - Minimum Receiver Lengths to Avoid Reflected Shock Waves from Contact Surface

The shock tube was fabricated from nominal 4.33-in. stainless-steel tubing of 0.083-in. wall. The maximum over-all internal length is 20 ft., which can be distributed between the driver and receiver sections as desired. Sections are held together by bolt flanges. Marman clamps were originally used to join some of the sections but these were removed because of our inability to achieve vacuum tight joints with them.

Photographs of the facility are given in Figs. 13 through 15. Figure 13 shows the complete facility, the slave end of the tube being close to the viewer, and the driver end back into the picture. In this view, the main instrumentation is to the right foreground. The aerosol generation equipment, consisting of the pump system and QL storage system, are also shown. The cylinders containing the gases for forming the detonation product gas-air mixture are shown in the left foreground. The small glass cylinder, shown on the table at the end of the tube, is the evaporator used to vaporize the liquid components of the detonation product gas to form a complete mixture in the shock tube. At the far end of the tube are the cylinders and plumbing for filling the driver section. Running along the tube is a copper pipe exhaust manifold used to evacuate the system. The vacuum pump exhaust is carried by pipe and discharged outside the building.

The data pickups for the shock tube work are two pressure transducers and a photocell unit. The pressure transducers are used to measure shock velocity and establish time relationships. The photocell provides us information on the combustion occurring in the system.

The pressure transducers are of the quartz piezoelectric type, Model 601 A, made by Kistler Instrument Corporation. They are used with Kistler Model 566 electrostatic charge amplifiers. The signals from the charge amplifiers are fed to a Model 727OR Berkeley Time Interval Meter which will give a direct digital readout of the time interval between passage of the shock wave past the two transducers. The signal from the transducer nearest the receiver end of the tube can also be fed to a type RM 45A Etkronix Oscilloscope through an electronic switch. This permits direct observation of the pressure-time history behind the reflected shock. The oscilloscope display is photographed with a Hewlett-Packard Model 196A Polaroid oscilloscope camera. The photocell unit is an 1P28 photomultiplier in a cathode-follower circuit. The photo cell is mounted on the receiver end of the tube and observes down the central axis of the tube. This permits observation of light output within the shock tube (ignition and/or combustion events). This signal is also fed to the oscilloscope through an electronic switch. The electronic switch will be used to sample the input signal from two signal sources and display them on a single-beam oscilloscope on a common time base. Alternatively, a dual beam scope can be used, eliminating the need for the switch.

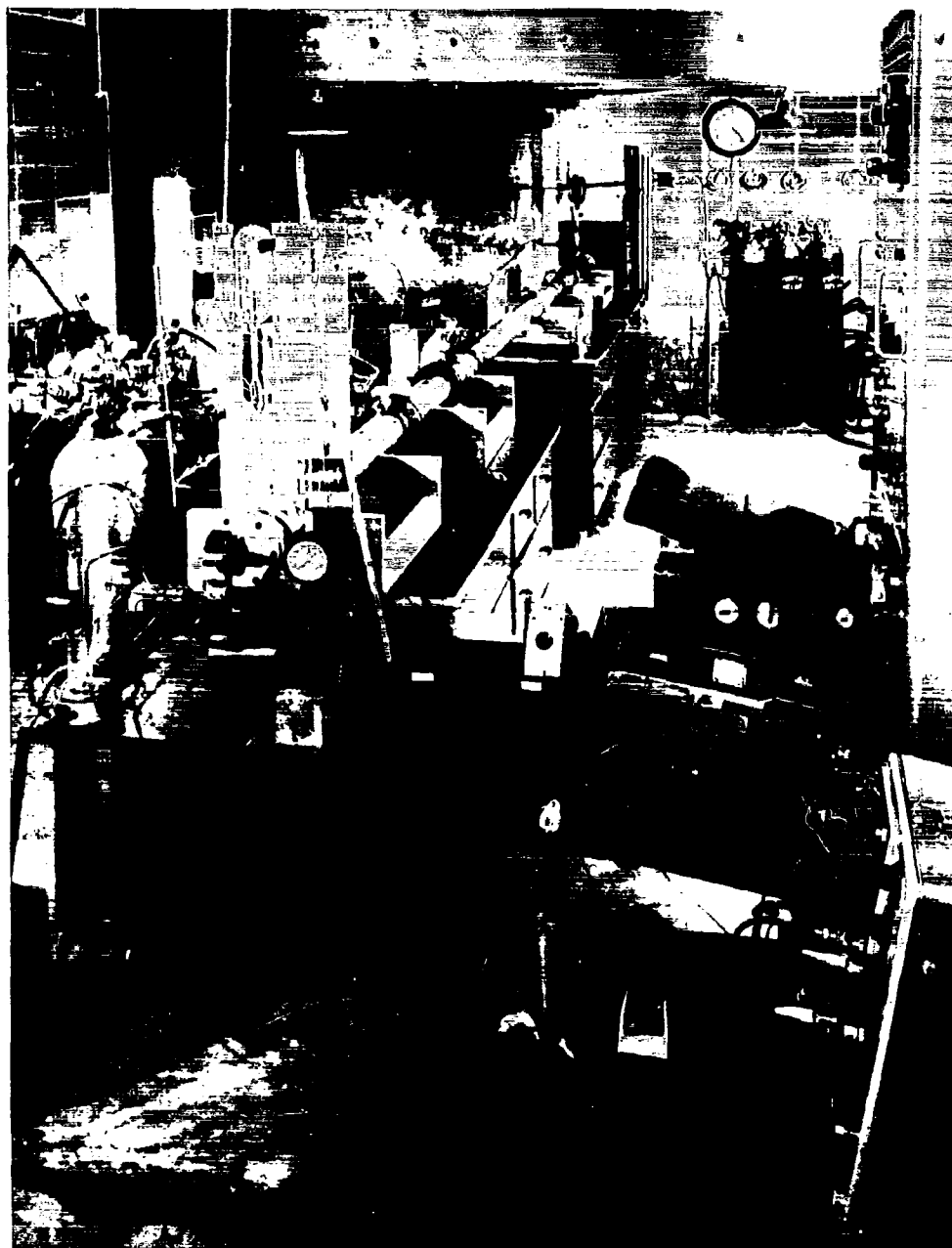


Fig. 13 - Over-All View of 4-in. I.D. Shock Tube

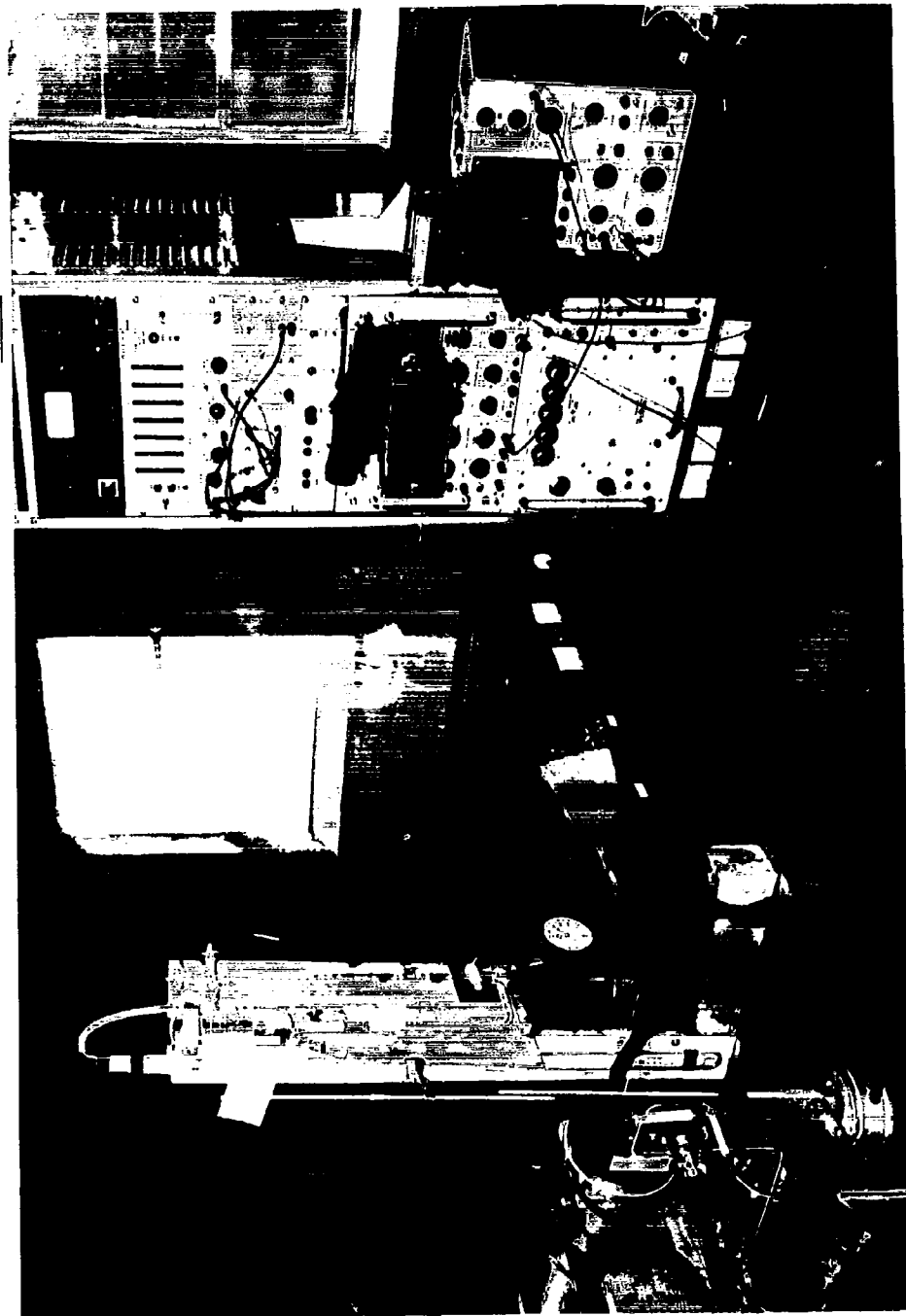


Fig. 14 - Instrumentation for 4-in. I.D. Shock Tube

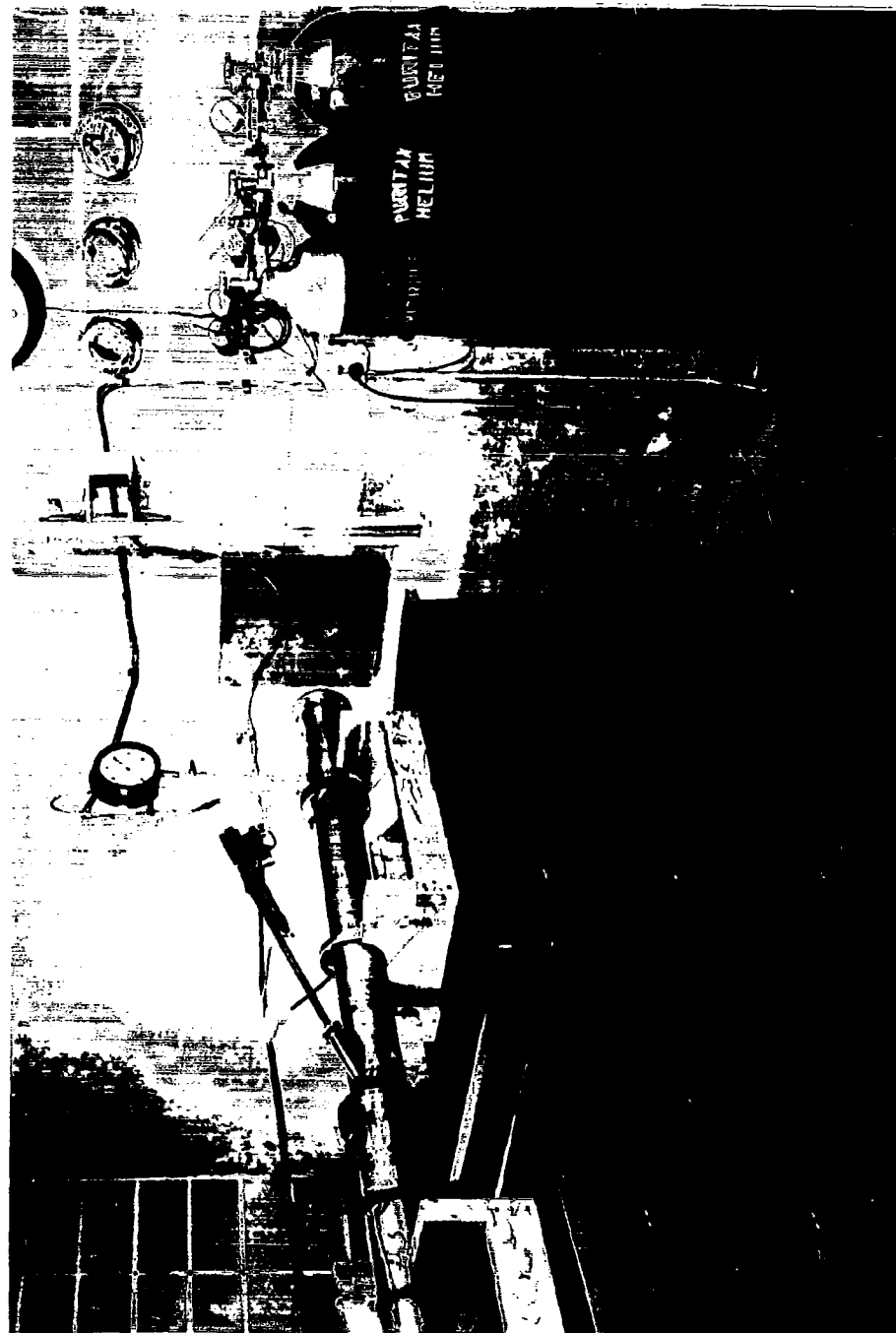


Fig. 15 - Driver Section, 4-in. I.D. Shock Tube, Showing Device for Breaking Diaphragms

The instrumentation can be seen in Fig. 14. The photomultiplier tube housing can be seen on the end of the shock tube at the extreme left. The Kistler charge amplifiers (only one shown) are mounted on a table just to the right of the injector pump. The next instrument is part of the low voltage photocell power supply. The rack mounted instruments are as follows. Starting at the top is the photocell high voltage power supply, the time internal meter, the single beam scope, a time delay generator, and another regulated power supply. At the right of the rack is a Tektronix dual beam oscilloscope.

The aerosol in the receiver section will change with time as particles coagulate and settle out. Therefore, it is desirable that the aerosol age, at the time of shock wave passage through it, be a controlled condition. To achieve this, one must be able to rupture on command the diaphragm separating the driver and receiver sections. Several methods of doing this have been used by others. Diaphragms which break at a predetermined pressure are frequently used but in this size and pressure range they cost \$20 each. Sparks are used to burn holes in the diaphragm, but this might ignite the flammable mixtures. Mechanical plungers are also used to perforate the diaphragm but these can be expensive and utilize a large part of the cross-section area which interferes with the gas flow. Squibs can be used but their cost is \$0.60 to \$1.25 each and squibs create a spark problem. Our solution was to use a Crossman air rifle to shoot a lead pellet at the stressed diaphragm. This reduced the equipment cost to \$21, and cost to rupture a diaphragm to a fraction of a cent.

The installation of the CO<sub>2</sub> gun can be seen in the photograph of the driver end of the shock tube, Fig. 15. The driver section pressurization gas is also fed to the gun. Diaphragms are cut from standard brass shim stock. Used diaphragms can be seen hanging on the wall in the photograph.

## V. EXPERIMENTAL DATA

### A. Particle Size Determination

An important part of the program is the establishment of a known aerosol particle size. Studies by Burgoyne<sup>10</sup> and co-workers have shown that when a liquid aerosol particle size is below about 10 $\mu$ , a combustion wave in such a mixture behaves like one in a premixed vapor-air system. Above about 40 $\mu$ , the particles were observed to burn individually in their own air envelope. Burgoyne and co-workers have also shown that the flammability limit is particle size-dependent. With small particles the lower limit approaches the lower



limit of the vapor-air mixture. With large particles (above  $40\mu$ ) the lower limit is about 18 mg. fuel/liter. This corresponds to distances between particles of about 31 times the droplet diameter which is slightly larger than the radius of the theoretical air sphere required for particle combustion.

A study by Kamo and Werle<sup>11/</sup> has shown similar results for high-boiling-point fuels. There is some indication that the particle size which produces the lowest flammability limit is on the order of  $100\mu$  at a fuel concentration on the order of 18 mg/liter. These data tend to show that with these high-boiling fuels, flame could be transmitted over larger distances between particles. This conclusion is hard to justify in view of the data of Burgoyne. The scatter in the data is fairly wide (which is understandable in view of the difficulty in working with aerosols) and the true position of the curves may be closer to the results of Burgoyne, or vice versa.

To eliminate ambiguity in determining in which of the two regimes we were operating, we selected two particle sizes as desirable for study, those below an arithmetic mean diameter of  $5\mu$  and those above  $100\mu$ . To generate these particle sizes in both the combustion chamber and the shock tube, we proposed to use a diesel fuel injector nozzle. Two Bosch nozzles were purchased: a No. ADN 15S2 and a No. ADN 15S3. Material is supplied to these nozzles with a Bacharach Nozzle Tester, Model YFL. This is a hand-operated positive displacement pump which will supply to the nozzle 0.95 ml. of liquid per stroke at a maximum pressure of 5,000 psig.

The particle size of the aerosol can be adjusted by varying the size of the nozzle and the operating pressure. A No. AKB-355-59P Bosch Nozzle Holder is used to adjust the pressure. This holder contains an adjustable check valve which prevents opening of the nozzle until a preselected pressure has been obtained. This insures that all flow through the nozzle occurs at the desired pressure. The pump also has a check valve which permits the entire flow system to be pumped to the set pressure of the nozzle. Once the system is at the desired pressure, the next stroke of the pump delivers fluid through the nozzle.

Particle-size studies were initiated in the combustion chamber using a water-glycerin mixture which has the same viscosity as QL. The study was initiated with water-glycerin to avoid a loss in time pending receipt of QL. The studies were made using the method of K. R. May<sup>12/</sup> which consists of measuring the diameter of holes caused by droplets in a magnesium oxide coated slide. Slides were placed coated side toward the injector nozzle at eight different levels in the chamber. In addition, two slides were placed "edge on," one at the top and one at the bottom of the chamber.

As a first step, pressures of 2,000, 3,000 and 4,000 psig were evaluated with the ADN 15S2 nozzle, which is the larger of the two. The arithmetic mean particle diameter decreased regularly as the pressure increased, as shown in Table IV. Since the smaller nozzle should produce smaller particles, an attempt was made to leap ahead by evaluating the particle size produced by the 15S3 nozzle (smaller of the two) at 5,000 psig. In addition, to get larger particles, the 15S2 nozzle was operated at 500 psig and the resulting particle size determined. The results of these experiments are shown in Table IV.

TABLE IV  
PARTICLE SIZES AS A FUNCTION OF PUMP PRESSURE

<u>Nozzle Pressure</u> <u>(psig)</u>	<u>Nozzle</u>	<u>Arithmetic Mean</u> <u>Particle Diameter</u> <u>(μ)</u>
500	15S2	~ 356
2,000	15S2	23.0
3,000	15S2	20.7
4,000	15S2	12.8
5,000	15S3	16.8

The particle size for the 15S2 nozzle at 500 psig is shown as approximate because several of the slides were so heavily coated that they could not be read. However, the average of the six slides counted indicates that the size is greater than that desired.

The data on the 15S3 nozzle at 5,000 psig confound our prediction. The particle size observed is larger than that obtained from the larger nozzle at a lower pressure.

At this point QL became available and the particle size studies were continued with this material.

The initial trial runs at 4,000 psig injector pressure disclosed that we were not getting any particles to the top of the chamber, in contrast to our experience with the glycerine-water mixture. It also disclosed that we apparently had a wider spread in the particle sizes than we had been experiencing with the glycerine-water. This meant that we had two new problems: (1) a change in the size distribution, and (2) a change in the distribution of particles within the chamber. The arithmetic mean particle size appeared to be about the same as with the glycerine-water mixture.

Originally, it was the intent of the project to characterize the aerosol produced by a known technique, which was to be within acceptable size limits. At this point, our problem reversed itself and became one of finding a technique to produce an acceptable aerosol. The problem was attacked in three ways: first, we secured the advice of senior MRI staff members through a formal briefing followed by an intensive discussion period; second, we contacted injector manufacturers and others for recommendations; and third, we instituted a much more rigorous technique for appraising the aerosols being produced.

The MRI senior staff presentation resulted in the recommendation that the nozzles and pump be evaluated with diesel fuel to determine if the problem was associated with some unusual feature of QL's liquid properties. It was also recommended that the nozzle spray angle be changed and that the combustion chamber spray distribution pattern be examined. However, the over-all view was that the approach being taken was sound and that the project should continue on its present course of action.

The American Bosch Arma Corporation was contacted to obtain recommendations on a nozzle which would produce smaller particles. After several discussions it was recommended that we try either an ADN 8SD24/4462 modified to an annular area of 0.23 mm. or an ADN 15SD35/4463 modified to an annular area of 0.13 mm. Both of these were ordered. These nozzles fit the original nozzle holder and are operated with the injector pump.

American Bosch Arma further stated that the reproducibility of our sprays would be improved if we used a mechanical pump system rather than our manual injection technique. They also stated that some improvement in particle size could be gained by going to pressures higher than 5,000 psig, our present limit.

The 8SD24 nozzle was evaluated first because the included angle of the spray with this nozzle is only 8 degrees. It was believed that this would improve the throw of the spray and assist in obtaining a uniform aerosol in the chamber.

A particle size analysis and a spray distribution study was made on this nozzle with 5,000 psig pressure on the injected liquid. Using QL it was found that 50 per cent of all spray particles were below 10 $\mu$  in diameter and 80 per cent were below 20 $\mu$ . The spray pattern in the chamber was good. The aerosol generated remains airborne; the walls of the chamber remain dry.

Pending receipt of the 8SD24 nozzle, an evaluation was made of the particle size produced in QL and diesel fuel sprays under similar conditions. It was found that the diesel fuel spray particle size was indeed smaller but that the particle size and particle size distribution in both sprays was similar.

It was decided that the spray produced by the SSD24 nozzle was close enough to the desired small particle size to initiate the aerosol flammability study in the combustion chamber.

#### B. Combustion Chamber Studies

Our approach to this problem dictated the establishment of flammability limits of the detonation product gas-air mixture, QL-air mixture, and the detonation product gas-QL-air three component system. It was hypothesized that much could be learned from the behavior of the three component system interaction. In addition, the ability of various types of ignition sources to ignite the system were also to be evaluated.

1. Detonation product gas-air flammability: To check the validity of the data to be determined, we ran initial experiments with methane-air mixtures for comparison of our upper and lower limit data with literature values.

Coward and Jones in Bureau of Mines Bulletin No. 503 report that the methane-air upper and lower limits in similar equipment are 5.75 and 13.6 per cent methane, respectively. Our data in the combustion chamber show that the lower limit is between 5 and 6 per cent and the upper limit between 13 and 13.5 per cent. Mixing was accomplished by allowing the air to "jet" into the partially evacuated chamber containing only methane, and then waiting 30 min. for additional diffusive mixing. The data show good agreement for this type of measurement, especially considering the lack of assurance of absolute mixing.

Measurements were then made on the synthetic detonation product gas. The detonation product gas was formed from both tank gas and vaporized liquids, as described earlier. The upper flammability limit of this mixture was found to be between 52.5 and 55 per cent of the gas by volume with air. The lower limit is between 22.5 and 25 per cent gas by volume with air. The interval between the two percentages does not represent the limit of our ability to measure the accuracy of the limit mixtures. They are only the last points in successive determinations of halving the difference between mixtures which "fired" and mixtures which "did not fire." We believed that determinations to within 2.5 per cent were sufficient for our purposes at that time.

It is possible to calculate flammability limits of multicomponent systems if the limits of each component are known. The method is given in Bureau of Mines Bulletin 503, which is also the most extensive single source of flammability data. As a further check on the accuracy of our data, we made a calculation of the limits of this gas mixture. The calculated lower limit was 22 per cent and the upper limit 55 per cent, which is excellent agreement with our experimental values.

Later in the program, after we had had started the evaluation of QL aerosols, we experienced a permanent shift in the lower limit of this mixture. In our investigation of this shift, we examined each and every possible contributing factor. None of the factors associated with possible changes in gas composition, mixing, or mode and manner of ignition were found to have changed. Changing gas cylinders or the liquid ingredients did not make the slightest difference in shifting the limit back to the original value. At present, we suspect contamination of the chamber surface as the most likely cause.

2. QL aerosol-air mixture flammability: Approximately 1.56 ml. of QL will form a stoichiometric mixture (carbon oxidized to  $\text{CO}_2$ ) with the volume of air contained in the combustion chamber if there are no other fuel gases present. This is equivalent to 0.106 gm/liter. It would be expected that the lower flammability limit would be on the order of 0.050 gm/liter and the upper limit about 0.180 gm/liter. At the small aerosol particle size (if the QL were vaporized) these values would correspond to 0.475 per cent and 1.72 per cent by volume respectively, at standard conditions.

QL aerosol-air mixtures were formed in the chamber using the injector system. The quantity of QL injected was varied by changing the number of pump strokes and/or limiting pump stroke travel. The pump normally delivered 0.95 ml/stroke.

In our first experiments we found, as predicted, that the spark ignition system being used in the combustion chamber would not ignite any QL-air mixture generated by the injector nozzle-aerosol generation system.

We proposed to ignite this mixture by introducing a flame into the system. Our first effort consisted of placing a thoroughly premixed 10 per cent methane in air mixture in a plastic bag balloon, which just filled the end of the chamber. This mixture was ignited by the spark igniter. We did not obtain any aerosol ignitions using this technique. We suspected that most of the "ignition" energy was going into disintegration of the plastic envelope. Rather than pursue this approach by adjusting the oxygen content of methane-air mixture to increase the strength of the ignition, we elected to try using an open flame.

A commercial "home workshop style" propane-air torch, utilizing bottled propane, was modified so that its aspirating air supply was provided independent of the burner environment. This was done so that the torch would continue to burn even in a closed system.

QL aerosol-air mixtures were created in the chamber using the injector system. The initial experiments were conducted by closing the chamber with a diaphragm consisting of single thickness of Saran wrap, injecting the QL into

the air filled chamber, and then inserting the burning torch into the system through the diaphragm. The torch was adjusted to give a 3 in. long flame with the multi-orifice tip. The system was judged flammable if a flame front propagated from the torch down to the chamber bottom.

The aerosol concentration was varied in small increments from 0.026 gm/liter to 0.26 gm/liter. No mixture tested met the present criteria for flammability. There was no doubt that the QL was combustible. Ignitions were observed in almost all instances, particularly in the range of concentration where this material was predicted to be flammable. What we did observe was that apparently the combustion products strongly inhibited the flame propagation. The flame front usually propagated about 2 to 8 in., accompanied by the production of copious quantities of dense smoke. Whenever this cloud reached a given density (visual observation) the flame was suppressed. It was frequently noted that this cloud of products extinguished the ignition torch, even though this was a premixed flame with an independent air supply. The color of the ignition torch in the presence of the aerosol and combustion products cloud changed from the characteristic blue to brilliant white-orange, with a slight green tinge. Other experiments were tried as follows. We attempted to evaluate flammability by injecting the QL aerosol into the chamber in the presence of the burning torch. The results were essentially the same with this exception. At low and medium concentrations, i.e., about 0.07 gm/liter and below, the spraying jet from the injector was ignited. This immediately flashed over the outer spray jet "surface", down to the injector orifice, before the aerosol cloud could expand laterally to the wall. This again is indicative of the combustibility of QL.

We conducted another experiment in which we evaluated the combustibility of QL as a free jet in the air. We took the generation system outdoors, and tried lighting the aerosol jet from the injector with a propane torch as it expanded into free air. In this instance, the jet burned at all points downstream from a given point of ignition, but the flame front did not propagate back toward the injector past the point of ignition.

In another test we observed that QL will burn quietly and completely in an open "pan fire", although it is difficult to ignite due to the low vapor pressure.

Realizing that requiring downward propagation as a test of flammability is a very severe criterion, we attempted to make some measurements with upward propagation of the flame front. A sheet metal chamber was constructed, similar in size and shape to the Plexiglas chamber. The new chamber had a port in the side to allow insertion of the torch and a thick glass top for observation of combustion. The results were essentially the same as those observed in the other chamber. Tests were made both (a) with the torch present during injection and (b) inserted after aerosol injection.

3. Three component flammability data: Having measured the detonation product gas flammability, determined the aerosol particle size and injector spray characteristics, we undertook the three component QL-detonation-product gas-air flammability study.

To determine the flammability limits of the three component mixtures, it is necessary that one component be held constant while the other two are varied. We elected to hold the quantity of QL constant in a given determination and vary the detonation product gas-air mixture to determine limits. The procedure was as follows: Taking one pump stroke of QL (0.95 ml.) as an initial constant quantity of aerosol, we injected this into a gas mixture and activated the spark igniter. The result was rated either "fire" or "no fire" depending on whether or not flame front propagated to the bottom of the chamber. Knowing the flammability limits of the detonation product-air mixtures alone, we could then judge in which direction to change the relative concentration of these two gases to obtain a result opposite to the first one, i.e., if we had a "fire" we next attempted to get a "no fire" mixture. The establishment of a "bracket" defined that the limit being sought was somewhere between these two values. By subsequently halving the difference between any two dissimilar results (fire, no fire), the position of the limit could be successively approached. After determining the limit for one QL concentration, we then changed to another and repeated the determination of limits by changing the gas mixture. Thus, all possible values and interrelationships of the three variables in the system are systematically examined.

The upper and lower flammability limits of the system can be examined in an identical manner. One only has to realize that as you move continuously in one direction along a constant concentration line of one component, the system will change from nonflammable to flammable and back to nonflammable.

The raw data thus consist of a series of gas mixtures containing a liquid-phase concentration of an aerosol. To present these data, we have elected to convert all values to mole per cent. This corrects the gas volumes for day-to-day variations in pressure and temperature and at the same time places all three components on a comparable footing.

The flammability data obtained are plotted in Fig. 16. Figure 16 is a plot of the detonation product gas and QL concentration only. The air concentration is equal to 100 minus the sum of these two components. In the normal case, it would be expected that if two flammable components in a system competed equally for the oxygen, the limits would correspond to an area defined by straight lines drawn between the respective limits of the components with air alone. In other words, it should be an additive property of the system. This is the principle which allows multicomponent system limits to be calculated, as we did for the detonation product gas mixture. Expected limits are shown as dashed lines on Fig. 16.

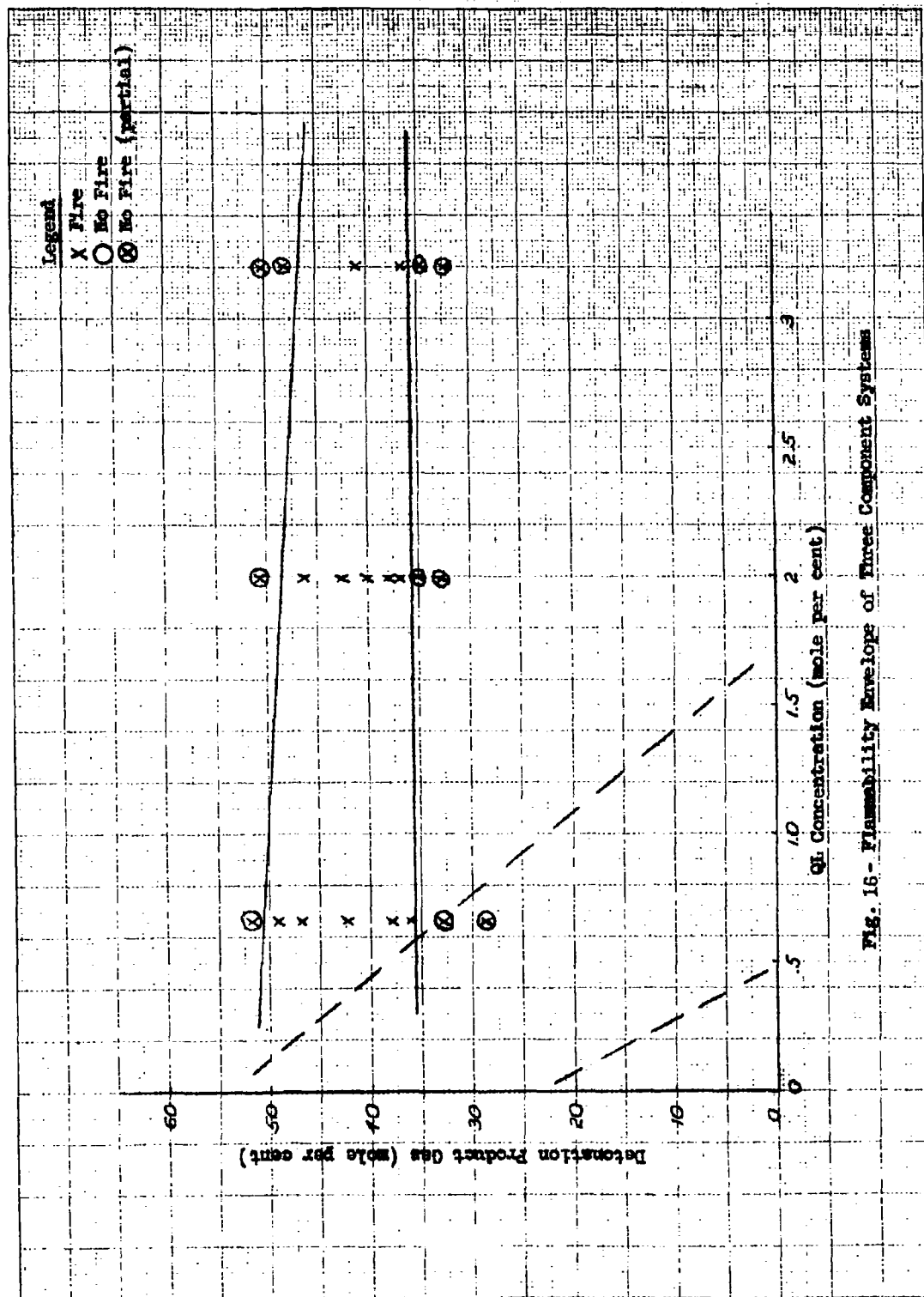


Fig. 16 - Flammability Envelope of Three Component Systems



The observed limits do not correspond to the expected limits. This is one of the most important facts derived from this entire project to date. The lines drawn indicate that the system flammability is virtually independent of the aerosol concentration. In fact, part of the apparent decrease in flammability at high aerosol concentrations is only due to the fact that the mole percentages have to add up to 100. The real ratio of the gas phase components remained essentially the same.

The position of the curves reflects the change in the detonation product gas-air mixture flammability referred to earlier. The QL is a solvent for the Plexiglas chamber wall and the wall becomes very sticky. We suspect that combustion products of the QL have become imbedded in the chamber surface and that this has changed the limits. A good soap and water scrubbing improves but does not eliminate the situation. This has certainly affected the quantitative value of the data but we do not believe that it should change the qualitative result, which at this stage of the program is the most important.

Observation of the combustion reveals that the flame propagation velocity of the mixture is greatly reduced in the presence of the aerosol. The flame propagates at a roughly estimated one-third normal velocity compared to detonation product-air mixtures alone. The color changes from the normal blue to orange. The flame front changed from planar to cellular. Large quantities of characteristic smoke were formed, although not as much as observed when burning the QL-air aerosol alone.

#### C. Shock Tube Studies

Construction and installation of the shock tube facility presented the usual rash of small problems inherent in the establishment of such a system. A number of leaks in weld joints had to be isolated and corrected. Some of the flange joints required refacing after welding to correct warpage. All in all, the problems were minor.

The diaphragm rupturing CO<sub>2</sub> gun has only been partially satisfactory. The principle is sound and the system as installed works well up to 200 psi pressure in the driver. Above this pressure, the unmodified gun vents the driver section pressurizing gas back through the mechanism. The pellet firing mechanism utilizes gas at high pressure; approximately 1,200 psi. However it discharges this gas through a restricted orifice with the orifice and firing mechanism metering the quantity of gas used to propel the pellet. Above 200 psi in the gun barrel, the pressure differential across the propelling gas is too low to impart enough energy to the pellet to rupture the diaphragm.

Limitations in time prevented our being able to do little more than undertake a set of preliminary experiments. The results are interesting and important.

Our initial observations were made without waiting for complete instrumentation. However, we observed that under the conditions we were operating that we were obtaining shock induced incandescence in air alone as well as light output from the detonation product gas-air mixture. We were not able to determine by eye if what we were observing in the gas mixture was combustion or shock incandescence.

Mounting the photocell disclosed that the gas mixture light output was much greater in amplitude and much longer in duration than shock incandescence in air. The oscilloscope trace of the photocell output disclosed the characteristic sharp rise and long tail-off characteristic of a combustion reaction in such a system.

The next questions we were interested in were (1) is the combustion initiated by the incident or reflected shock, and (2) what is the true shock velocity? The Kistler pressure transducers were supposed to answer these questions as well as to determine the ignition time delay.

Installation of the transducers and their respective amplifiers disclosed that one amplifier was inoperative. This was returned to the manufacturer for repair. Our interim capability was reduced to one transducer which eliminated our ability to measure shock velocity directly. Calculated values from the gas pressure ratios are given in the data below.

We found that, according to prediction, the combustion ignition was occurring behind the reflected shock. Figure 9 is used to determine the temperature of the gas mixture when ignition occurs. Varying the shock strength to determine the fire-no-fire condition will indicate the temperature at which autoignition occurs in the system.

We were able to obtain data on both the detonation product gas-air system and on the three component system before the end of the program. We selected a mixture in the middle of the flammable range for this work, namely 40 per cent product gas and 60 per cent air. We found that reflected shocks of Mach 3 and 3.8 but not Mach 2 would ignite this mixture. We took this same gas mixture and dispersed about 0.75 gm. of QL per liter in it and found that this mixture would ignite at Mach 2.5 but not at Mach 2. Data are available on only those shock strengths specifically named.

The equipment has been shown to perform for the task intended. It has proven that moderate shock strengths can cause ignition in this type combustible system.

#### D. Hot Particle Ignition

An investigation was made of the ability of hot particles to cause ignition in the three-component aerosol mixture. All tests were made in the combustion chamber using a mixture composed of 40 per cent by volume detonation product gases and 60 per cent air, in which the QL concentration was 0.065 gm/liter.

The method of injecting the hot particles was very simple. We made up a "puffer" out of high pressure pipe, a rupture diaphragm assembly, a solenoid valve, and a small high pressure gas cylinder. The original concept was to charge the gas cylinder to a known pressure and isolate it with the solenoid valve. Downstream of this valve was a 6-in. section of 1/4-in. schedule 80 pipe, closed at the exit end with the rupture diaphragm assembly. The sample to be injected was placed in the section of pipe and heated with a propane torch. An insulated and shielded chromel P-alumel thermocouple was welded into the system so that direct measurement of temperature in the powder bed could be obtained.

The 325 psi rupture diaphragm was supposed to allow pressurization of the powder bed after heating and rapid injection of the material into the chamber upon catastrophic failure of the diaphragm. In practice we could not differentiate between operation with and without the diaphragm; so we dispersed with it, injecting the powder through a 1/8-in. diameter orifice at the end of the pipe. This orifice was closed with a cork during heating to prevent oxidation of the powder sample.

Three materials were studied: aluminum, iron and charcoal. A summary of the tests is given in Table V. The maximum metal powder temperature studied was limited by the metal powder melting point.

As stated in the table, no condition studied was able to cause ignition. It should be noted that the carbon injected burned in the gas mixture without setting off an ignition.

TABLE V

## HOT PARTICLE IGNITION

[illegible]

### E. Combustion Inhibition Studies

The study of combustion inhibition did not progress very far during this program. We were able to evaluate  $\text{CCl}_4$  and found that less than 1 per cent by volume in the gas phase would suppress ignition and combustion of the three-component aerosol mixture.  $\text{CCl}_4$  was selected because of its known specificity for carbon monoxide combustion suppression. We had planned to contrast its effect with  $\text{CH}_3\text{Br}$  as an added indication of whether or not CO combustion was the dominant feature of this system.

## VI. DISCUSSION AND CONCLUSIONS

### A. Experimental Results

This program has made a major advance in the over-all problem of achieving a solution to the agent flashing problem. We initially proposed that the presence of the detonation product gases were of major importance to the problem and we have proven our contention. We have shown that consideration of the flammability of an agent aerosol in air is too limited a viewpoint and that it ignores what is probably the main culprit, i.e., combustion of the detonation product gases with air.

Reviewing our originally proposed model of the system, we find that the new data support the initial hypothesis that the ignition source for the aerosol is the combustion of the detonation product gas mixture. We have not as yet proven the further step that, in general, aerosol combustion occurs only during the detonation product gas combustion but our observations also support this concept.

The data on Fig. 16 offers dramatic evidence that a low vapor pressure material in aerosol form does not play a major part in system flammability. The liquid phase is an unsuccessful competitor for the oxygen in the air. The QL aerosol is not significantly involved with the transfer of the flame front through the system.

The shock tube studies have shown that a shock wave of moderate strength is capable of igniting the system. A BRL report<sup>13</sup> has shown that Mach shocks of sufficient magnitude to cause ignition exist for long periods following detonation. The shock tube is capable of delivering much additional information of value to the program. For example, it should be possible to obtain precise ignition temperatures of any combustible system. The effect of changing any of the system factors can be evaluated comparatively quickly.

This would enable one to determine the value of changing the detonation product gas composition. By examining the time duration of combustion with and without the aerosol phase, we should be able to learn more about whether the aerosol contributes materially to the combustion. Mass balances before and after combustion can be obtained to determine the extent of aerosol participation. The shock wave should be considered as a temperature pulse, capable of initiating many important phenomena.

The hot particle studies have indicated that under the conditions of the test this is not an important ignition source. The fact that the carbon combusted without igniting the mixture is indicative of the resistance of the system to this type ignition.

The difficulty observed in burning QL-air aerosols is also indicative of the fact that aerosol combustion may only occur (in the general case) in the presence of the detonation product gas combustion. Large droplet diffusion flame type combustion would be particularly suppressed when the combustion products are combustion inhibitors.

#### B. Use of QL

The use of QL on this program introduced a number of complicating factors, the most important of which are the materials compatibility problem and lack of standardized technique for its analysis. Lack of a proven analytical technique caused us to abandon attempts to analyze for undecomposed material in our combustion study. However, despite the difficulties and the problems and delays it created, we believe that its selection was a wise choice because of the added meaningfulness it gave to the data. It was worth the cost.

#### C. Aerosol Generation

Production of high concentrations of nondispersed aerosols is a tough problem. Our attempt was based on the use of diesel fuel injectors and we achieved a good degree of success. To our knowledge, this was the first time that concentrations high enough to give upper limit flammability data have ever been obtained. In that respect we have set a new milestone.

There are still many opportunities for improvement. Higher pressures should be studied. The system should be converted from manual to a mechanized operation for greater reproducibility. Further efforts should be made to characterize the system. Attention should also be directed toward other aerosol generating systems. Use of Astrosonics, Inc., accoustical nozzles should be considered.

## VII. RECOMMENDATIONS

The present type of study should be continued so that the effect of changing the physical properties of the aerosolized material, i.e., flash point, vapor pressure, etc., can be determined. It is predicted for example, that with high vapor pressure materials the flammability of the fuel components of the system will become additive, other factors being equal.

Aerosol materials which can be easily analytically analyzed for should be studied to determine the degree of aerosol participation in the combustion events. Thought should be given to using materials or agents which are involved in the flashing problem, to verify the conclusions obtained to date.

Since one approach to flashing inhibition is to prevent the aerosol phase deterioration, regardless of what happens in the balance of the system, aerosol combustion and ignition suppressants should be studied with the view of incorporating them into the liquid phase.

The attempt to identify possible ignition sources and rate them according to their probability should be extended. The shock tube will enable determination of the ignition temperature required as factors in the system are systematically varied. Thus changes in the detonation product gas mixture can be evaluated to determine the effect this variable has on ease of ignition. Similar effects can be studied varying aerosol phase vapor pressure, molecular structure, additives, etc.

The aerosol generation system should be re-examined with the aim of improving its performance. Operation, automation and increased pressure are recommended. Consideration should be given to a continuous flow system so that mixtures can be stabilized before ignition. Either the diesel fuel injector or the Astrosonics acoustic nozzles could be used in such a system. The Astrosonic nozzles should be examined to determine if they offer better performance than the diesel injectors.

Finally, a problem beyond the scope of this study is that of improving techniques for characterizing aerosols. This is an old problem and a continuing effort should be exerted until routine methods for the quick, accurate and easy characterization of aerosols are determined.

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# SYMBOL LIST

$P_1$  = Receiver pressure

$P_2$  = Pressure behind incident shock

$P_3$  = Driver pressure

$P_4 = P_2$  = Pressure behind contact surface

$P_5$  = Pressure behind reflected shock

$C_1$  = Velocity sound in receiver gas

$C_2$  = Velocity sound in receiver gas behind incident shock

$W_A$  = Velocity of incident shock

$W_B$  = Velocity of reflected shock

$T_1$  = Receiver temperature

$T_2$  = Temperature behind incident shock

$T_3$  = Temperature of driver gas

$T_4$  = Temperature of driver gas during expansion

$T_5$  = Temperature behind reflected shock

$U$  = Velocity of gas

$t_0$  = Time expansion wave hits head end of driver

$t_{fi}$  = Time at which expansion wave head, reflected from end of driver, is coincident with tail of expansion wave

AD _____ Accession No. _____ Midwest Research Institute, Kansas City, Missouri INVESTIGATION OF THE FLASHING OF AEROSOLS - Alan R. Pittaway Final Report, 20 April 1964, 66 pp., 16 illus., 5 tables Contract DA 18-108-AMC-118(A)	AD _____ Accession No. _____ Midwest Research Institute, Kansas City, Missouri INVESTIGATION OF THE FLASHING OF AEROSOLS - Alan R. Pittaway Final Report, 20 April 1964, 66 pp., 16 illus., 5 tables Contract DA 18-108-AMC-118(A)	1. Aerosols* 2. Chemical warfare agents 3. Aerosol generation*	1. Aerosols* 2. Chemical warfare agents 3. Aerosol generation*	1. Aerosols* 2. Chemical warfare agents 3. Aerosol generation*
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